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Study of the changes in optical reflectance relative to oxide film thickness

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STUDY OF THE CHANGES IN OPTICAL REFLECTANCE RELATIVE TO OXIDE FILM THICKNESS

by

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ABSTRACT

When an aluminum surface is exposed to an intense source of ultraviolet light, the "natural" oxide growth on that surface is accelerated. In addition, the thickness of that oxide film exceeds the thickness which would grow under "normal" conditions, i.e. normal room temperature and atmospheric conditions. When the aluminum surface is a reflector, the reflectance in the ultraviolet range is known to decrease with an increase in oxide film thickness. The decreasing reflectivity with increasing oxide film can be modeled mathematically.

This paper shows that the reflectance loss due to the irradiation of an aluminum reflector is not consistant with a mathematical model based solely on an increase in oxide film thickness.

STUDY OF THE CHANGES IN OPTICAL REFLECTANCE RELATIVE TO OXIDE FILM THICKNESS

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CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

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ABSTRACT

When an aluminum surface is exposed to an intense source of ultraviolet light, the "natural" oxide growth on that surface is accelerated. In addition, the thickness of that oxide film exceeds the thickness which would grow under "normal" conditions, i.e. normal room temperature and atmospheric conditions. When the aluminum surface is a reflector, the reflectance in the ultraviolet range is known to decrease with an increase in oxide film thickness. The decreasing reflectivity with increasing oxide film can be modeled mathematically.

This paper shows that the reflectance loss due to the irradiation of an aluminum reflector is not consistant with a mathematical model based solely on an increase in oxide film thickness.

INTRODUCTION

Historical Origin of the Problem

Over the past few years aluminum surfaced, nickel reflectors have been used at the Western Electric Engineering Research Center for concentration of high intensity mercury-xenon arc lamp radiation in heating studies on various work pieces. The reflecting surfaces were made by the vacuum deposition of about 2000Å of aluminum on the nickel base and overcoated with amorphous silica evaporated by an electron gun method. This overcoating was applied immediately after the aluminum was deposited without breaking the vacuum in the chamber. The overcoating was applied to serve several purposes. It provides a mechanical protection which allows the surface to be cleaned. It also provides increased reflectance in the far-ultraviolet region, according to Denton Vacuum, Inc., the company that vacuum deposited the coatings. The effect of overcoating reflector surfaces is discussed in the literature (1, 2, 3).

These studies were plagued by the rapid deterioration of the reflecting surfaces. The deterioration was first noticed by the drop in integrated power as determined by a thin-foil radiometer placed in the position of the work piece. An examination of the surface revealed areas of change in appearance and what might be termed "crazing." The whole reflector did not take on this appearance. The original analysis of the problem led to the conclusion that ozone generation by the lamp in some way caused the degradation. In subsequent experiments, the cooling gas for the high intensity lamp was changed to

nitrogen to provide a more inert atmosphere for the system. This failed to correct the problem. At this point, the study was put aside.

To define the degradation, a section was cut out of one of the degraded reflectors and its surface was studied by the use of both a scanning electron microscope and by replicating the surface and using a conventional electron microscope. Figures 1 and 2 are micrographs of replicas taken from this surface, which is an aluminum surface with an evaporated silica overcoating. The degradation is the result of 20 hours exposure to a 600 watt xenon lamp in what might be termed a normal laboratory atmosphere. Figures 3 and 4 show micrographs of the replicas of the nickel surface beneath the degradation. The aluminum and silica layers were removed by etching with hydrofluoric acid. The micrograph in Figure 5 shows an unexposed reflector surface treated with etchant as above. These observations will be discussed later.

Further search in the laboratory notebooks revealed that not all reflectors deteriorated as quickly as this one did. In addition, not all reflectors used in the studies deteriorated.

In an effort to determine the cause of this deterioration a set of experiments were designed using one inch nickel discs prepared and coated by the same commercial suppliers as the original ellipsoidal reflectors--nomminally by the same processes.

It was considered possible that the nickel surface or the nickel-aluminum interface may have been responsible for the degradation. Therefore, a special reflecting disc was prepared with a layer of evaporated silica between the nickel substrate and the aluminum

surface. To get a more complete study, four types of surfaces were exposed to the intense radiation of 1000 watt mercury-xenon lamp. These were a plain nickel substrate, a nickel substrate with only the aluminum coating applied, a nickel substrate with both the aluminum and the silica overcoating and the special reflector made by isolating the aluminum from the nickel with silica and overcoated with silica. These four types of samples were then exposed under carefully controlled conditions which were similar to those that had degraded the original reflectors.

The silica overcoated discs showed no signs of degradation after 462 hours, however, the uncoated aluminum surface became hazy and its reflectance diminished noticeably. The bare aluminum sample was examined using a scanning electron microscope. The micrograph may be seen in Figure 6.

Statement of the Problem

The topic of this thesis investigation has been selected based on these observations. Specifically, the purpose of this study is to investigate the effect of exposure of uncoated, front surface aluminum reflectors to an intense mercury-xenon light source on the ultraviolet reflectance of that surface.

BACKGROUND

It is well established that the reflectance of the surface of evaporated aluminum deteriorates in the ultraviolet range below the wavelength of 2000Å upon exposure to air (5, 6, 7). It is also reported that the primary cause for this loss in reflectance is the formation of a thin oxide film on the reflecting surface (6, 7, 8). Berning, Hass and Madden (6) have shown that the oxide film on freshly evaporated very high purity aluminum grows to 10-12Å after one hour of exposure to air. It reaches 15Å after the first day and almost ceases to grow after a month when it is about 22Å thick. This oxidation rate is considerably lower than those reported elsewhere (8, 11) and is attributed to super-pure aluminum and extremely fast evaporation which forms a smoother film. Therefore, the reported value of about 40Å (8, 11) will be used as the "maximum" thickness of the "natural" aluminum oxide film on samples such as ours prior to their exposure to the light source. The rate at which the self-protecting film grows is logarithmic (9, 10) at room temperature and may appear asymptotic (9). The samples used in this study were over 6 months old and are assumed to have reached a point where there will be little if any additional "natural" growth of aluminum oxide.

The wavelength of interest in this study is 3250Å and in this range the oxide film is considered non-absorbing (6).

Experimental studies by Walkenhorst (11) and later Cabrera, Terrien and Hamon (12) have shown that upon irradiation with ultraviolet light, the growth rate of aluminum oxide on aluminum increases.

The thickness of the aluminum oxide also exceeds that which grows naturally. Walkenhorst attributed the additional growth in film to the presence of ozone produced by the strong ultraviolet radiation. Cabrera, et al point out that the oxidation process is diffusion controlled by the Al^{+++} ion and is therefore independent of the partial pressure of oxygen and is therefore also independent of the presence of ozone. In reference (13) Cabrera presents an hypothesis on how the intense radiation from a light source can increase both the growth rate and the final thickness of the oxide film. The ultraviolet radiation disturbs the electronic equilibrium between the metal and the oxide by increasing the number of electrons being emitted from the metal surface. This requires essentially photoexcitation over a barrier approximately equal the work function of the metal. The correction for the electron affinity of the oxide is generally small. This requires, $h\nu > \varphi$ where

h = Plancks constant

ν = Frequency of the light

φ = Work function of the metal

The value assumed by Cabrera for the work function of aluminum was approximately 1 eV and the $h\nu$ of the mercury arc lamp was about 4 eV which satisfied the condition. The interaction of these added free electrons with the Al^{+++} ions increases the diffusion rate of the Al^{+++} and O^{--} and thus increases the growth of the oxide film.

In this study, ellipsometric measurement of film thickness are employed and thus a dependable set of optical constants of the material involved is necessary. The optical constants usually employed are the index of refraction (n) and the absorption coefficient (k). The constants are functions of the wavelength and angle of incidence of the light and have been determined by a variety of methods (14, 15). Ruiz-Urbietta, et al, (15) performed experiments using a helium-neon laser as a light source to measure thin film thickness. Since the instrument employed in this study used the same type of light source, the values of (n) and (k) (at .6325 microns) were taken from that study.

In order to interpret the effect of oxide film growth on the reflectance, an expression for the reflection coefficient is required. Using such an expression curves were calculated which plot absolute reflectance vs. oxide thickness as functions of the optical constants. The curves were calculated using a program provided by D. T. Moore of the Western Electric Research Center. This program was devised by P. W. Baumeister (16) to solve the equation

$$R = \frac{a_1 \cos^2 \delta_1 \times a_2 \sin^2 \delta_1}{a_3 \cos^2 \delta_1 \times a_4 \sin^2 \delta_1}$$

where

$$a_1 = (n_1 - n_3)^2 \quad , \quad a_2 = [(n_2 - n_1)\ n_3/n_2\ ]^2$$

$$a_3 = (n_1 + n_3)^2 \quad , \quad a_4 = [(n_2 - n_1)\ n_3/n_2\ ]^2$$

λ = wavelength of incident radiation

n_1 = index of refraction of air

n_2 = index of refraction of a thin film

n_3 = index of a refraction of a substrate

$\delta_1 = \frac{2\pi\ n_2 t}{\lambda}$, t = thickness of thin film

The optical constants for aluminum and aluminum oxide presented a problem at the wavelength of the reflectance measurements (λ = .325 microns). There are a variety of values for (n) and (k) for the same materials at about the same wavelengths, see reference (14). After examining the literature it was decided to use the values listed in Hass (3) in Table II for aluminum. This gave a value of n = 0.28 and k = 3.50. Aluminum oxide had values of n = 1.92 and k = 0. This list was used because the list was the most complete and numerically consistant for an increasing λ .

The effects of surface roughness on reflectance has been investigated by several experimentors (17, 18, 19, 20). Love and Francis (17) investigated the reflectance as a function of angle and

surface roughness in 302 stainless steel. The angles of incidence ranged from normal to 90°.

Three types of finishes were examined highly polished, mill finish, and sand blasted. After investigating reflectance at various angles of incidence, the conclusion was drawn that when the magnitude of the wavelength exceeds the surface roughness the surface becomes specular. When the wavelength is less than the roughness, the surface reflects some of the energy in off-specular directions and the surface appears diffuse in character. At about 60° all surfaces approach a specular surface. As summed up in the reference, the reflectance of any surface is dependent on three parameters, surface roughness, light source wavelength and angle of incidence. (No mention was made of surface film.)

The work done in determining the effects of surface roughness on the reflectance of radiant energy point out that the diffuse components of the reflected radiation will be determined by the condition of the surface. These diffuse components can be found by measurements of reflectivity at various angles of reflectance for a given angle of incidence.

A special type of surface roughness which has been studied (21, 22, 23) is termed "V-groove roughness." Torrance and Sparrow (23) modeled various types of grooves and their effects on reflected energy. From their study it was learned that the shadowing and masking of facets by adjacent grooves serve to diffuse the incoming beam by multiple scattering and by internal scattering.

This can put the off-specular peak at a variety of reflected angles depending on the angle of incidence, the structure of the V-groove and direction of the grooves in relation to the angle of incidence. In a discussion between K. E. Torrance of Cornell University (see Reference 23) and R. C. Pfahl, it was learned that the effect of the V-grooves parallel with the radiation source have not been modeled as yet.

The various influencing factors referred to here have been considered in this study. The effect of each as individual factors or all as combined factors will govern the final model of reflectance as a function of film thickness.

MATERIALS AND APPARATUS

The samples used in this study were one inch diameter nickel discs about 3/32 of an inch in thickness made by Foremost Manufacturing. These were made by the electrodeposition of nickel on an electropolished stainless steel mandrel. The mandrel was polished by Acme Scientific of Chicago, Illinois. The process is a combination of electropolishing and a mold polishing process. It has a trade name of Super-Lustre surfacing. The finished surface has a 0-2 micro inch (.500Å) peak-to-valley surface as a result of the process. This surface is the portion of the mandrel to which the discs were electroformed. The discs were then sent to Denton Vacuum, Inc. where 2000Å of 99.99% pure aluminum was deposited on the face surface of the disc.

A ring shaped stand was designed to support the reflectors for exposure to the radiation. It was designed to make certain all of the samples received the same intensity during the exposure to the Hanovia (Model 977B-1) 1000 watt xenon-mercury arc lamp. The lamp was supported in a vertical position in the center of the ring and could be moved in the x, y, and z directions (Figure 8).

The ring was provided with positions to hold eight samples at a time with an open position located in the lamp support region. At the open position a Model 30 Hy-Cal Radiometer was mounted to monitor the energy output of the source. A Model 8686 Leed and Northrup potentiometer was used to monitor the output voltage.

The thin-foil radiometer is a precision transducer. It is used to measure radiant energy distributions over a wide band of wave-

lengths extending from ultraviolet to infrared. It consists basically of a thin constantan foil suspended across a heat sink with a fine copper wire welded to the center of the foil. The heat sink is water cooled to allow continuous exposure to radiant energy.

The enclosure in which the samples were irradiated was made of Plexiglas with green ultraviolet absorbing polymer layer affixed to the exterior. This enclosure was provided with an air vent which exhausted the ozone produced.

An examination of the Plexiglas enclosure before this study was started revealed that some mechanism during the previous exposures (described in the Introduction) had degraded the interior walls of the enclosure. In addition, the PVC insulation on the power leads to the lamp had changed from white to brown and were no longer plastic in character. The Tygon tubing used to supply cooling air for the lamp and cooling water for the ring had also changed color.

Since it is known that ultraviolet irradiation causes these polymers to give off monomers or halide molecules, the exposure fixture was surrounded by a cylindrical shield of aluminum foil to prevent the intense source from irradiating the enclosure.

The monochromatic specular reflectance of the aluminum surfaces was measured using a reflectometer designed and built by Dr. R. C. Pfahl of the Western Electric Engineering Research Center, (24). It combines the energy source mount, the sample mount and the focusing optics into one unit all of which are mounted on a motor driven turntable (Figure 9). The optical system is shown

schematically in Figure 10. The reflectometer was designed to allow a continuous reflectance curve to be recorded for angles of incidence from 5 to 85 degrees. It was also designed to make absolute reflectance measurements. In this study, however, the mode of operation was changed to make relative reflectance measurements.

Incident angles of 10° and 65° were chosen purely as a matter of convenience. At these two angles, there were no obstructions in the optical path by the specially designed sample mount to be used for relative reflectance measurements. In addition, the path length through the oxide film at 65° was about 2.4 times as great as the path length at 10° so effects of film properties should be exaggerated.

The specially designed sample mount consisted of a unit which permitted two samples to be mounted in the reflectometer simultaneously (Figure 11). The sample mount fitted into a track on the sample table so that measurement of the reflectivity from both the sample and the standard was made by simply sliding the sample holder along the track placing the reflecting surface of interest in the optical path of the reflectometer. The same angle of incidence was assured by snugging up the thumb screw which forced the front of the sample holder tightly against the front of the track (Figure 11). The surfaces that slid on one another were machined surfaces and the precision of the angle of incidence depended on these machined surfaces. Once the standard reflectance sample, against which all readings were compared, was placed into position in the holder,

it was never removed throughout the study.

The detector system for the reflectometer consisted of a Perkin-Elmer Model 99 Double Pass Monochrometer coupled to a photo-mutiplier, the output of which was recorded on a Model G Leeds and Northrup Speedomax Stripchart Recorder.

For a source of energy, a hydrogen arc lamp was used as recommended by Perkin - Elmer for an energy source in the near ultraviolet range. The source was focused to a spot size of about 2 mm on the sample. This was chosen to average out any minute or isolated surface imperfections. Near ultraviolet was chosen since this was the area of most interest to the eventual application. A wavelength of .325 microns was chosen because of the stability of the light source and detector at that wavelength.

The aluminum oxide film thickness was determined by ellipsometry. A Gaertner Model L119 ellipsometer was used. The light source was a helium-neon gas laser, which provided a monochromitic light of 0.6328 microns. The detector was a photomultiplier coupled to an oscilloscope. See Reference 4 for a detailed discussion on ellipsometry.

EXPERIMENTAL METHOD

Prior to exposure of the samples to the intense light source, the relative reflectances of the samples were measured in the reflectometer. The samples were then mounted in the support ring for exposure. Filtered, dehumidified air was blown upward through holes around the base of the lower arc lamp electrode. This was done to carry off some of the heat developed by the lamp. The distance between the arc of the lamp and the sample faces was two inches.

The samples were removed periodically and relative reflectance measurements were taken. As the reflectance of the samples decreased by a predetermined amount, samples from the group were removed to a desiccator. These samples did not undergo further exposure. (When the standard sample was not being used, it also was kept in a desiccator still mounted in the sample holder.) The remaining samples were then returned to the exposure ring. This process of exposure and reflectance measurement was repeated until each of the samples reached the desired level of reflectance degradation.

In measuring the reflectance changes in the reflectometer, the samples were always placed in the sample holder in the same orientation. This was facilitated by an orientation mark scribed into the back of each sample.

Oxide film thickness measurements were then made on all the samples including the standard sample by ellipsometry. All samples

were assumed to have reached their room temperature limit of oxide thickness before the exposure study started.

The results of the ellipsometric measurements were then analysed by a computer using a program provided by R. O. DeNicola of the Western Electric Engineering Research Center. This program determined the thickness of the aluminum oxide film on the sample surfaces given the values of the optical constants of aluminum and aluminum oxide. The source of the initial values for n and k was Reference 15. The values were n = 1.577, k = 0.00036 for aluminum oxide and n = 1.21, k = 7.2 for aluminum. When these values were read into the program, they gave an unrealistic value for the room temperature oxide film thickness, i.e. 76$\overset{\circ}{A}$. Through the use of the computer program a set of optical constants for aluminum oxide were obtained which resulted in the thickness of the oxide before exposure of 43$\overset{\circ}{A}$. This seems more meaningful from the results reported in the literature (8, 11). The constants used were n = 2.2, k = 0.0004 for aluminum oxide and n = 1.21, k = 7.2 for aluminum.

A dry stripping technique was used to make the replicas of the reflector surfaces. A thin layer of 1% Formvar solution in ethylene chloride is dispersed over the sample and removed with cellophane tape directly onto a 3.0 mm copper grid. This is then placed in an evaporator where platinum and carbon are deposited at an angle of approximately 30°. The photographs in Figures 1 to 5 are the reverse images of the actual surface topography.

All measurements were repeated to establish the precision of

the data. The output reading of the reflectometer was repeated by sliding the sample mount back and forth to establish dependability on the method. The reflectance values were repeatable within $\pm$ .2%.

The accuracy of the resetting of the angle of incidence was not determined. What was done was to set the sample table to the desired angle and then rotate the reflectometer table to get the peak value. The scale on the table indicated it was in good alignment with the sample table but there was no way of knowing if either scale was accurate. The reflectometer is designed so the angle of incidence is equal to the angle of reflection and throughout the experiment this was assumed to be the case.

Once the monochromator was set to the wavelength of interest (.325 microns) it was not changed.

EXPERIMENTAL RESULTS

The results of the reflectance measurements made at 10° and at 65° angles of incidence are given in Tables 1-8 and Figures 13-16. At 10° there is the lack of a decernible trend in the experimental results. The curves for the 65° results indicate a similar curve shape. These curves are drawn in by eye as a "reasonable" representation of the average trend.

The ellipsometric measurements indicate an increase in film thickness with respect to time of exposure. This can be seen in Table 9 and Figure 18.

The scanning electron micrographs of Figure 12 indicate a smooth surface results from the exposure.

DISCUSSION AND CONCLUSION

As can be seen in Figures 13 to 16, all samples measured at 65° incidence display the same curve shape. The same samples measured at 10° display the same trends but the curves for relative reflectance at 65° may not resemble those for 10°. The tables of reflectance values for 10° (Tables 1 to 4) indicate there is a $\pm$ 4% difference in initial relative reflectance between sample 1 and 11. If a $\pm$ 4% error bar is placed on the data for 10° in Figures 13 to 16, all points will fall in a straight line range band. Therefore, no conclusion can be arrived at for the 10° data, and only the 65° data will be considered further.

Photographs A and B in Figure 12 are electron micrographs of an aluminum reflecting surface used in the experiment and exposed to ultraviolet radiation for 388 hours. At 10,000X and 50,000X there appears to be no topography which might lead one to believe that scattering could have a large part in the reduction of reflectivity.

The resolution of the scanning electron microscope is about 200Å. The light lines running horizontally through the photographs are raster lines. The secondary emission of electrons are produced in the first 100Å of surface. Since it is approximated that an 80Å film of oxide exists on the surface, some effect of the aluminum must be considered. What that effect is, is not known.

Intuitively, one might expect that of the two angles of

incidence at which measurements were taken, those taken at 65° would record the most effect of any surface change, with regard to oxide thickness increase. The path length in the oxide layer is about 2.4 times further at 65° than at 10°. The calculated curves of Figure 17 indicate a difference in reflectivity at these two angles but does not predict a significant dependence of reflectivity on thickness of the oxide layer. If the rapid decrease in reflectivity for $t < 100$ hours can not be accounted for by an increase in oxide thickness alone, other mechanisms must be sought. In analyzing the reflectance data at 65°, the computer program used to generate the theoretical curve was manipulated in an attempt to artifically create the observed time dependence. This was done by changing the absorption coefficient (k) to larger values. Originally (k) was considered to be zero but if the intense radiation to which the aluminum oxide was subjected actually changed the absorbing characteristics of the film, the changes in the program might be made to represent the data. This can be seen in Figure 19. The value of (k) at 40Å equaled zero and was increased to 0.7 at 50Å and was held constant at 0.7 through 80Å. This resulted in a rapid decrease in reflectivity between 40Å and 50Å with a linear decrease to 80Å. This is not the observed effect as seen in the experimental curve for sample number 11. To arrive at the curve labeled sample 11, the value of (k) would have to increase to a relatively high value (0.7) and then decrease continually to a value of about 0.4 at 80Å. There seems to be no reason to suspect

this is actually happening.

In Figure 18 is shown the actual growth rate of aluminum oxide with respect to time of exposure. This curve is the product of the ellipsometric measurement on all the samples. This is justified by the assumption that all the samples obeyed the same growth rate kinetics.

In examining the curves more closely, the curves for samples 2 and 7 at 65° have a higher relative reflectance than the curves for samples 1 and 11 (Figure 20 and 21). An investigation of the samples in oblique lighting revealed striations in the reflecting surfaces.

In measuring the reflectance changes in the reflectometer, the samples were always placed in the sample holder in the same orientation. This means the impingement of the light from the source was always from the same direction relative to this orientation. Any surface factor which influenced the relative reflectance measurement would remain constant--other than the increase in oxide film.

The striations on samples 2 and 7 were almost perpendicular to the direction of the incident beam in the reflectometer while those on samples 1 and 11 were almost parallel with the incident beam.

The literature states that at about 60° all surfaces become specular (17 - 20). Torrance and Sparrow (23) model random V-groove cavities and find surfaces of this nature also become specular at about 60°. Hering and Smith (22) show the incident energy reflected from an array of machined V-grooves having the same included angle and whose upper edges lie in the same plane, is concentrated at or near the angle of incidence.

It is apparent that the sample surfaces are not V-grooved in the strict sense since the reflected energy is greatest at an angle of reflectivity equal to the angle of incidence. The orientation of the striations does result in a difference in reflectivity but the shape of the curve which defines the reflectance loss is unaffected by the orientation of the grooves in the incident beam of the reflectometer.

An investigation into the origin of the grooves revealed them to be polish marks. In order to remove a stain or foreign matter which was deposited on the surface of the sample, the manufacturer buffed them with jewelers rouge. This resulted in the minute scratches which were duplicated by the deposited aluminum.

There is no doubt that there was a change in character in the film. This could be defined as a change in thickness or a change in properties. By holding the optical constants of aluminum and aluminum oxide constant in the computer program used for the ellipsometric readings, an oxide film growth is indicated. The other consideration would be that the oxide film remains constant and the optical properties of the aluminum oxide change. This would be contrary to the findings of both Walkenhorst (11) and Cabrera (13). However, some combination of these two effects may be the actual case.

An analysis was attempted using Bougers Law (25) for the absorption of radiation propagating through a medium.

$$\frac{I}{I_o} = e^{-\alpha t}$$

where I_o = the intensity of the radiation entering the medium

I = the intensity of the radiation after traversing a distance t through the medium.

t = thickness of medium in centimeters

$\alpha = \frac{4\pi k}{\lambda}$ given in cm^{-1}

k = absorption coefficient of the medium

λ = wavelength of radiation in centimeters

The results did not fit the experimental data.

From the data gathered in this study, the following conclusions can be made.

A. There is a measureable amount of film thickness increase which is consistant with Cabrera's data (See Figure 23).

B. The reflectance loss due to the irradiation of an aluminum reflector by an intense energy source is not consistant with the model of purely an increase in thickness of the oxide film.

C. A simple monotonic increase of the absorption coefficient of the aluminum oxide film with irradiation time will not fit the reflectance data.

D. There is evidence of the effect of the striations or polish marks on the relative reflectance. These can be seen in Figures 21 and 22.

FURTHER AREAS OF STUDY

Comparing Figures 3 and 4 with Figure 5 indicates some difference in nickel surface. The question is, was the change the result of the degradation or was the degradation the result of the rough appearance? Prior to exposure to the high intensity lamp, there was no visual indication of surface deformity. After exposure, the surface was visually degraded in addition to losing its high reflectivity in the ultraviolet range. The micrographs in Figures 1 and 2 show a bubbling effect on the surface. This also indicates that something beneath either the silica surface or the aluminum surface is acting to separate the reflector from the substrate. More study is needed in this area to determine the cause. This can be done by a study of the variables in manufacturing technique beginning with the polishing of the mandrel. Emphasis should be placed on knowing the condition of the substrate just prior to deposition of the aluminum coating.

This study should be repeated using optically flat glass as a substrate. In this way, any reaction effects between aluminum and nickel from the contaminants in the nickel would be eliminated. In addition, the optical constants of nickel would not have to be reckoned with due to the penetration of the radiation.

Since the use of jewelers rouge is of a general practice, the modeling of the surface effect should be undertaken if only to anticipate this form of reflectance loss.

CONCLUDING REMARKS

In comparing Figure 6 with Figure 12 a vast difference in surface topology can be seen. The sample in Figure 6 was exposed in the same atmosphere as the sample in Figure 12 with one change. The intense radiation from the lamp was not permitted to strike any of the polymeric substances in the exposure chamber. It can be concluded that non-uniform growth of surface material must in some way be coupled with the breakdown in polymeric material by the light source. The by-product from the degradation of the chamber material apparently had no effect on the overcoated sample used in the first experiments. This provides another reason for applying this protective overcoat other than a mechanical reason for surface cleaning.

TABLE 1
RELATIVE REFLECTANCE MEASURED AT 10°

Sample #1

Time Hours	Raw Relative Reflectance	Normalized Relative Reflectance
0	.987	1.00
6	.963	.975
21	.955	.9675
40	.949	.9615
63	.960	.9726
105	.952	.9645
132	.969	.9817
173	.954	.9665
190	.935	.9473
218	.957	.9696
267	.929	.9407

TABLE 2
RELATIVE REFLECTANCE MEASURED AT 10°

Sample #2

Exposure Hours	Raw Relative Reflectance	Normalized Relative Reflectance
0	.992	1.00
6	.956	.9637
21	.941	.9566
40	.968	.9756
63	.976	.9838
105	.961	.9687
132	.960	.9677
173	.952	.9597
190	.967	.9792
218	.961	.9687

Sample #4

0	.987	1.00
6	.969	.981
21	.969	.981
40	.949	.9615

TABLE 3
RELATIVE REFLECTANCE MEASURED AT 10°

Sample #7

Exposure Hours	Raw Relative Reflectance	Normalized Relative Reflectance
0	.961	1.00
6	.937	.9750
21	.939	.9771
40	.936	.9739
63	.960	.9889
105	.911	.9479
132	.945	.9771
173	.934	.971
190	.947	.985
218	.949	.9875
267	.915	.9521
388	.945	.9833

TABLE 4
RELATIVE REFLECTANCE MEASURED AT 10°

Sample #11

Exposure Hours	Raw Relative Reflectance	Normalized Relative Reflectance
0	.910	1.00
6	.892	.9802
21	.910	1.000
40	.911	1.0010
63	.913	1.0032
105	.890	.978
132	.925	1.017
173	.914	1.004
190	.913	1.0032
218	.912	1.002
267	.864	.9494
388	.905	.9945
410	.873	.9593

TABLE 5
RELATIVE REFLECTANCE MEASURED AT 65°

Sample #1

Exposure Hours	Raw Relative Reflectance	Normalized Relative Reflectance
0	1.024	1.000
6	.957	.9345
21	.941	.9189
40	.897	.8759
63	.867	.8467
105	.884	.865
132	.897	.8759
173	.882	.862
190	.868	.848
218	.875	.8545
267	.894	.874

TABLE 6
RELATIVE REFLECTANCE MEASURED AT 65°

Sample #2

Exposure Hours	Raw Relative Reflectance	Normalized Relative Reflectance
0	1.008	1.0
6	.982	.9742
21	.943	.935
40	.932	.9246
63	.890	.8829
105	.908	.9007
132	.903	.895
173	.916	.9087
190	.915	.9077
218	.901	.8938

TABLE 7
RELATIVE REFLECTANCE MEASURED AT 65°

Sample #7

Exposure Hours	Raw Relative Reflectance	Normalized Relative Reflectance
0	.973	1.0
6	.966	.992
21	.907	.932
40	.904	.929
63	.852	.8756
105	.866	.890
132	.871	.869
173	.882	.9064
190	.876	.9003
218	.864	.8879
257	.880	.9044
388	.891	.9157

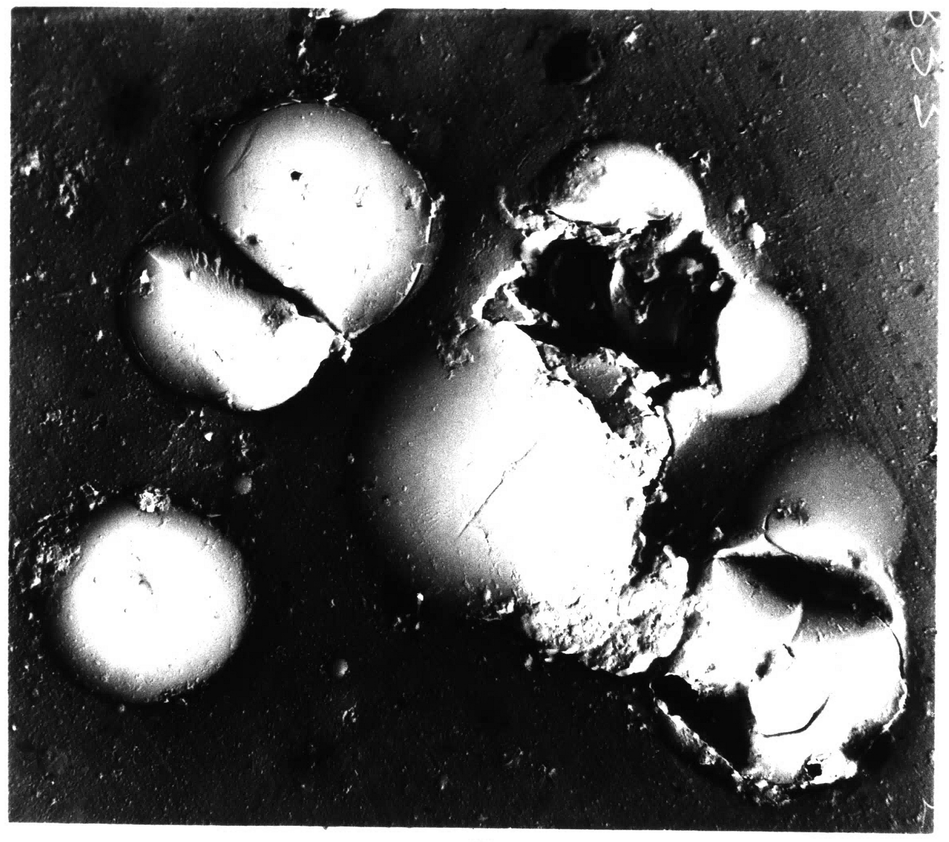
Sample #4

0	1.024	1.0
6	.947	.925
21	.960	.9375
40	.884	.863

TABLE 8
RELATIVE REFLECTANCE MEASURED AT 65°

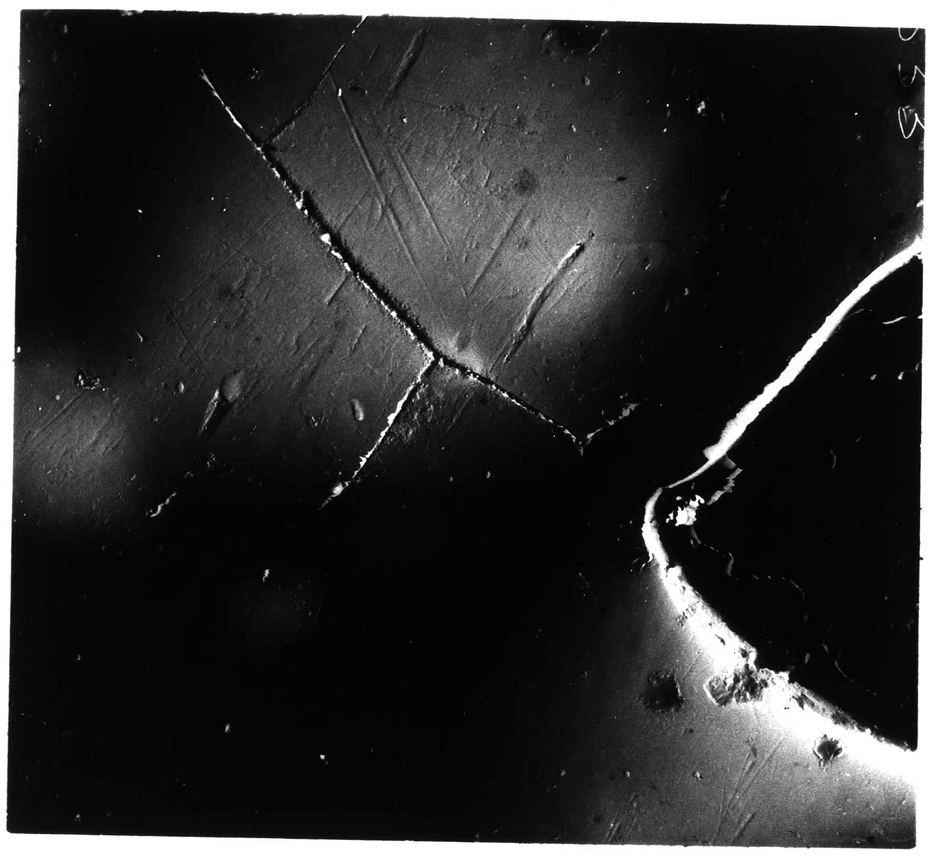
Sample #11

Exposure Hours	Raw Relative Reflectance	Normalized Relative Reflectance
0	1.000	1.000
6	.933	.933
21	.915	.915
40	.870	.870
63	.859	.859
105	.866	.866
132	.864	.864
173	.866	.866
190	.853	.853
218	.855	.855
267	.855	.855
388	.897	.897
410	.878	.878



DEGRADED REFLECTOR ORIGINAL 2400X

FIGURE 1

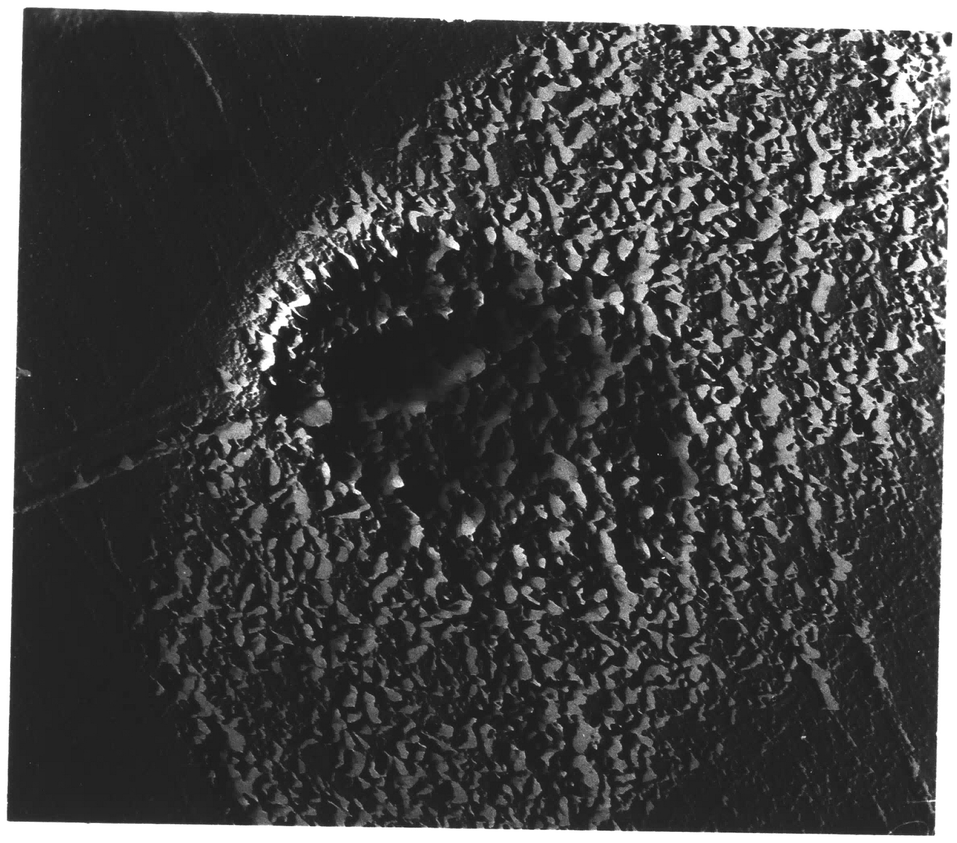


DEGRADED REFLECTOR ORIGINAL 2400X

FIGURE 2

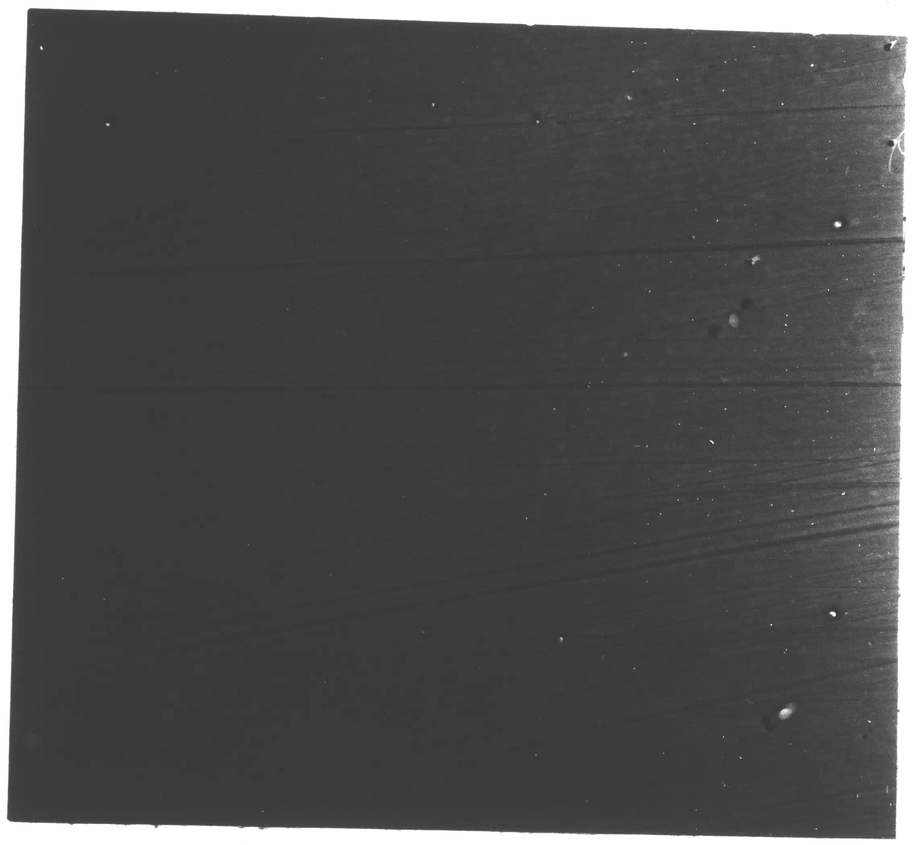
ETCHED REFLECTOR OF FIGURE 1 & 2 ORIGINAL 2400X

FIGURE 3



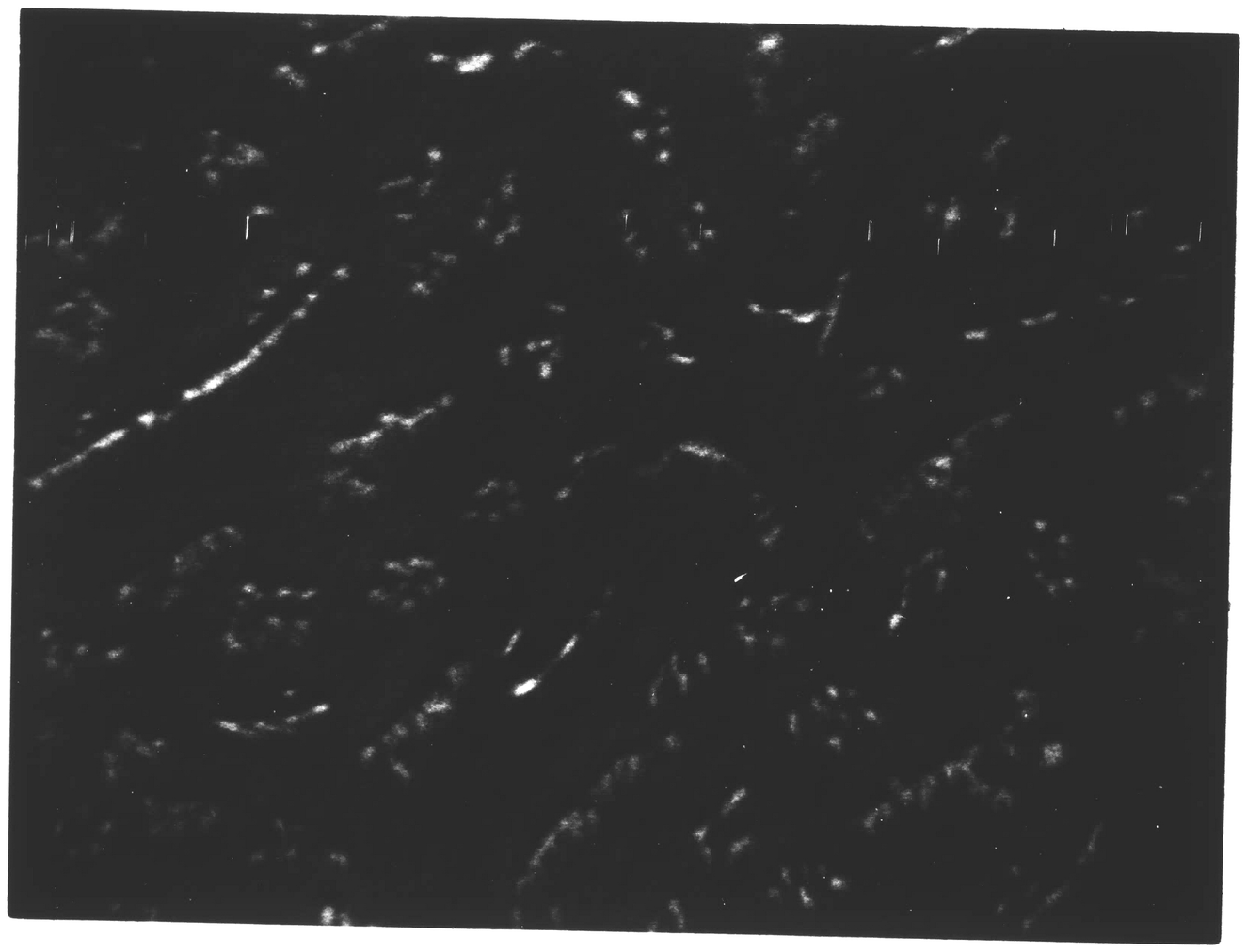
ETCHED REFLECTOR OF FIGURES 1 & 2 ORIGINAL 10,000X

FIGURE 4



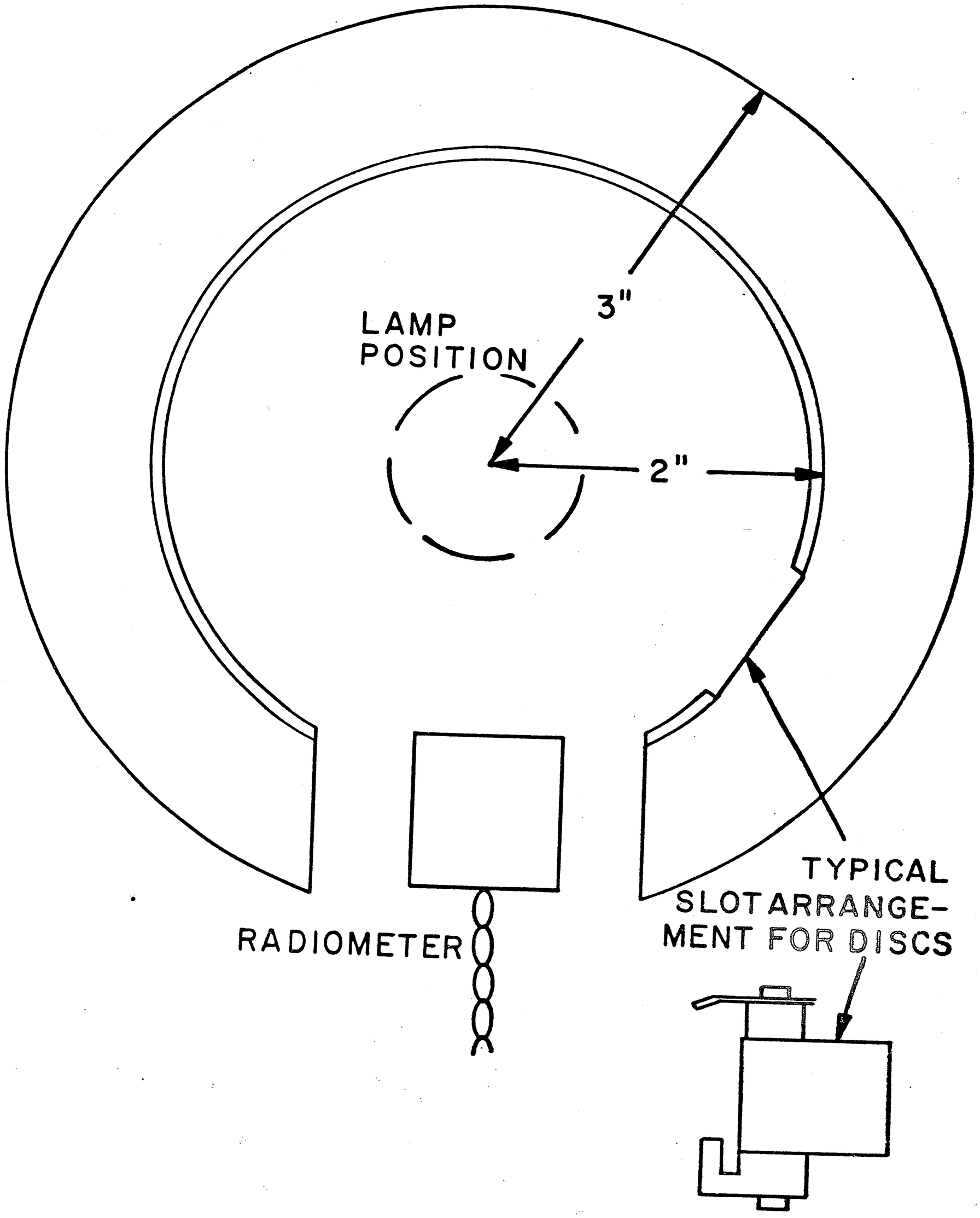
NICKEL SURFACE OF A GOOD REFLECTOR ETCHED TO REMOVE ALUMINUM AND SILICA ORIGINAL 2400X

FIGURE 5



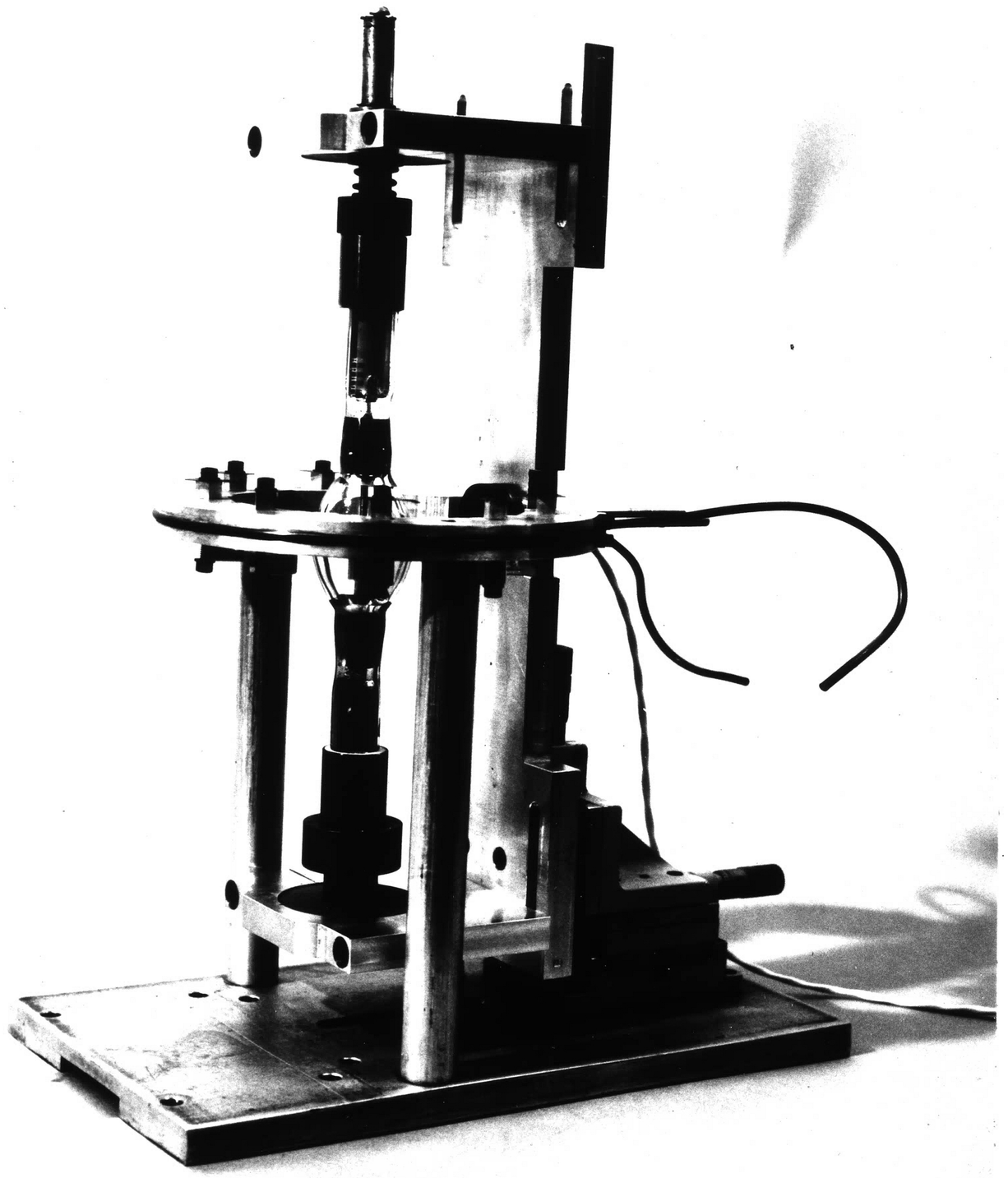
BARE ALUMINUM REFLECTOR AFTER 148 HOURS OF EXPOSURE
(1ST EXPERIMENT) ORIGINAL 5400X

FIGURE 6



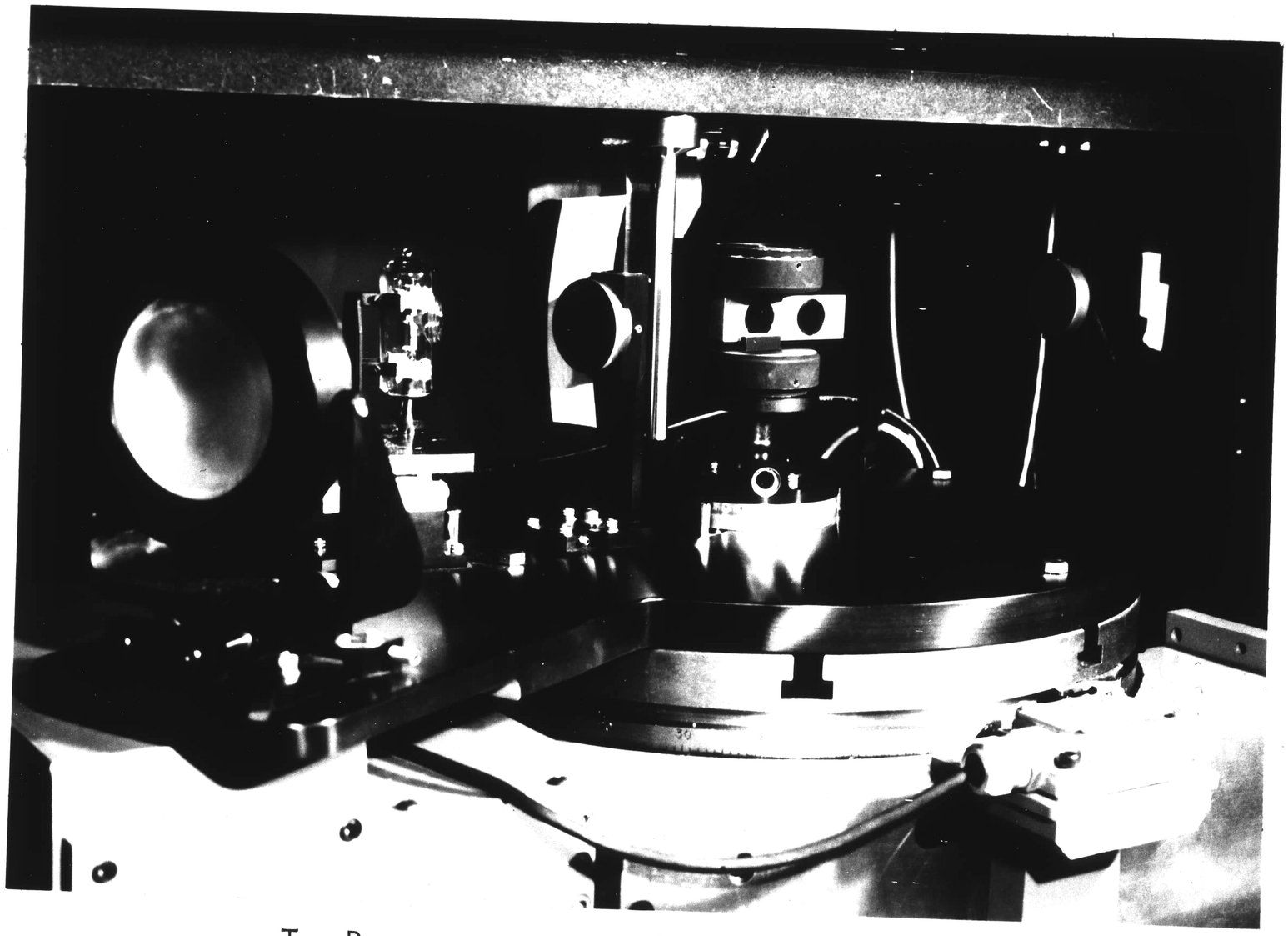
ALUMINUM EXPOSURE RING - 8 DISC CAPACITY

FIGURE 7



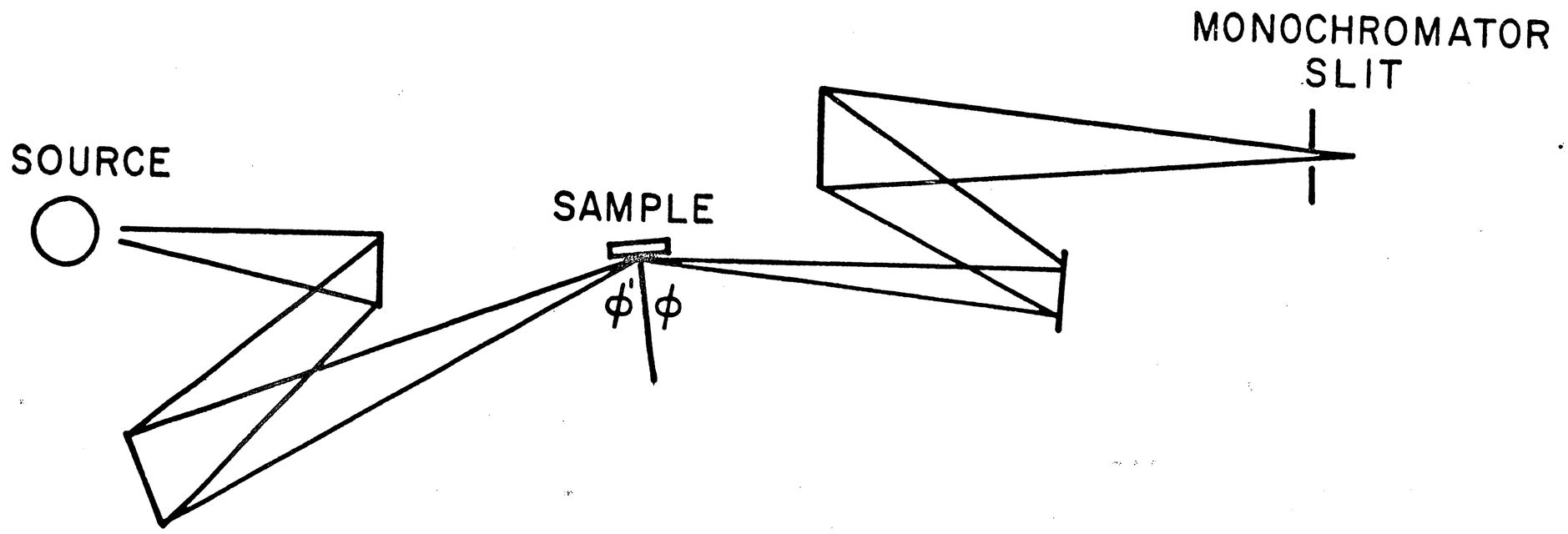
LAMP SUPPORT AND RING STAND

FIGURE 8



THE REFLECTOMETER WITH SAMPLE MOUNT IN PLACE

FIGURE 9

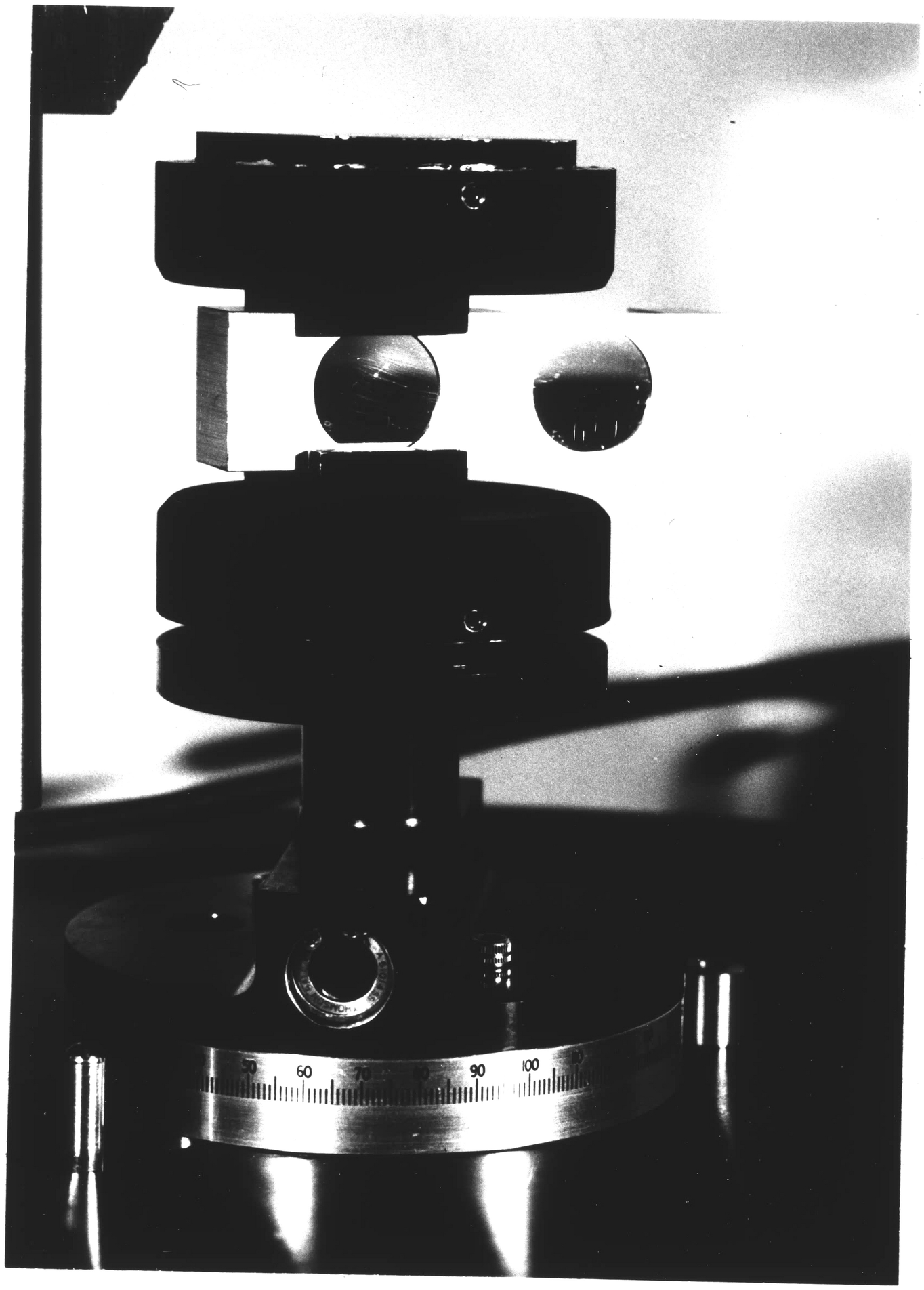


ϕ = ANGLE OF INCIDENCE

ϕ' = " " REFLECTION

SCHEMATIC OF REFLECTOMER OPTICS

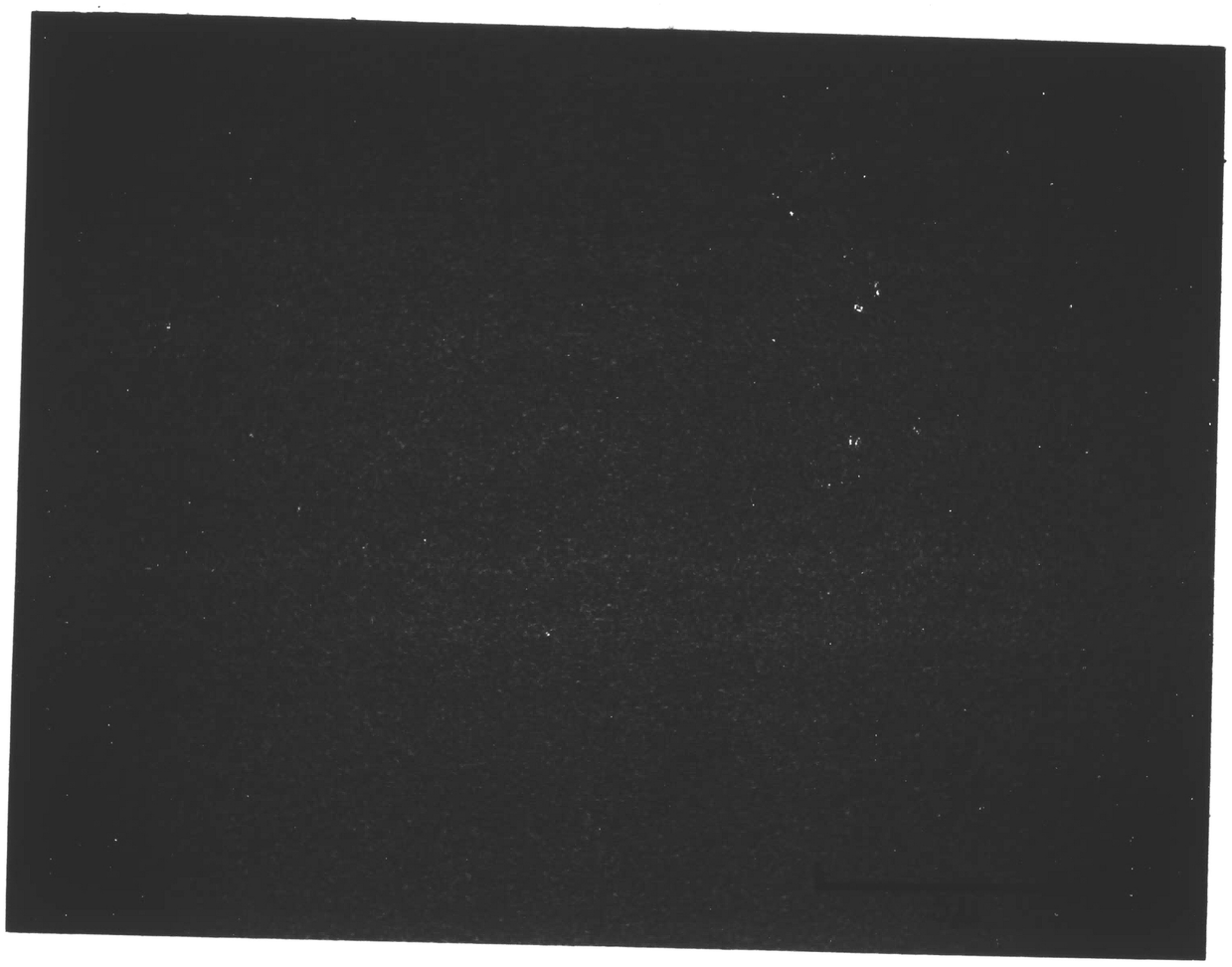
FIGURE 10



SAMPLE MOUNT SHOWING SLIDE TRACK

FIGURE 11

A ORIGINAL 10,000X



B ORIGINAL 50,000X

MICROGRAPHS OF SAMPLE #7

AFTER 388 HOURS

EXPOSURE TO LIGHT SOURCE

FIGURE 12

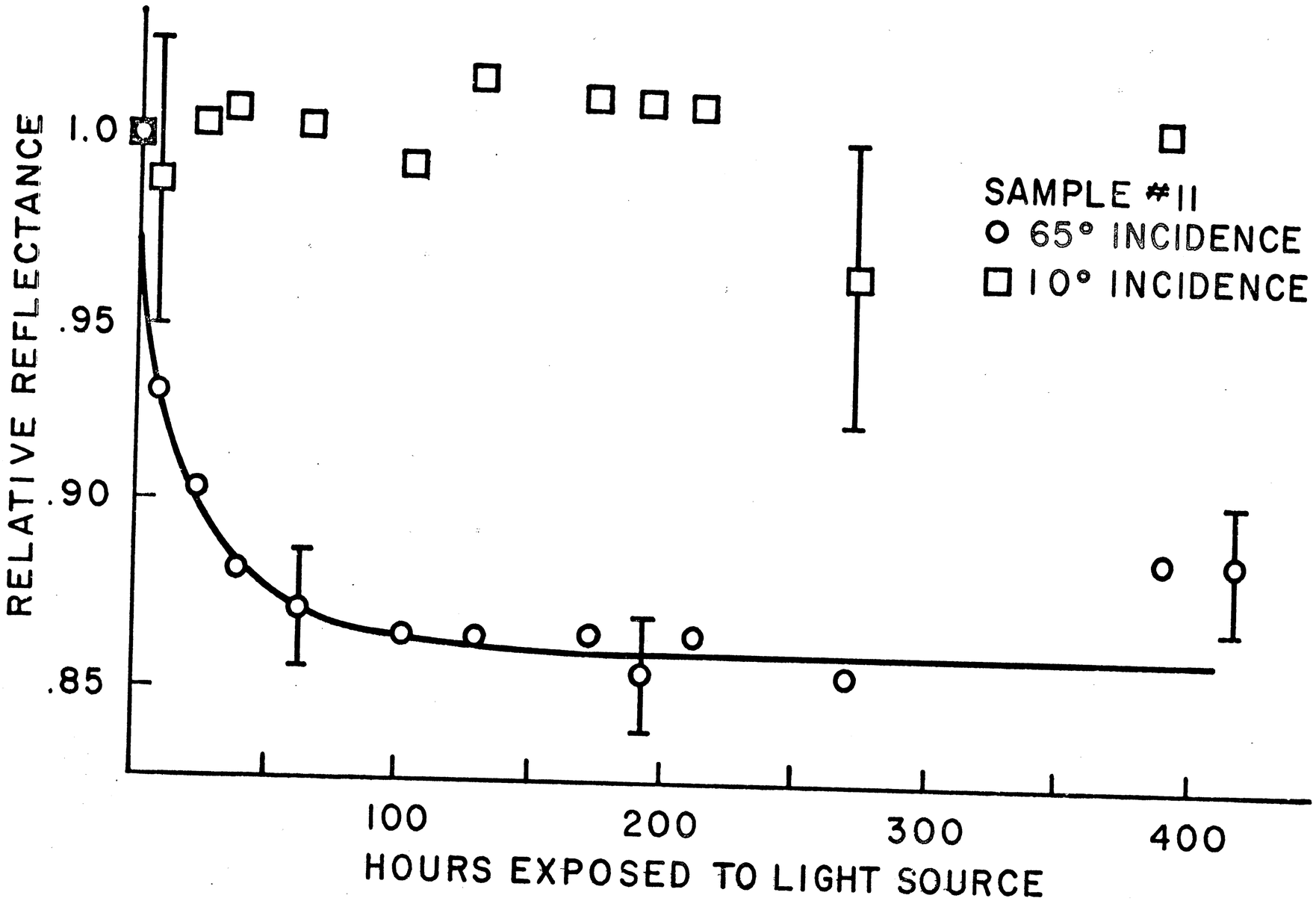

RELATIVE REFLECTANCE
1.0
.95
.90
.85
100
200
300
400
HOURS EXPOSED TO LIGHT SOURCE
SAMPLE #11
65° INCIDENCE
10° INCIDENCE

FIGURE 13

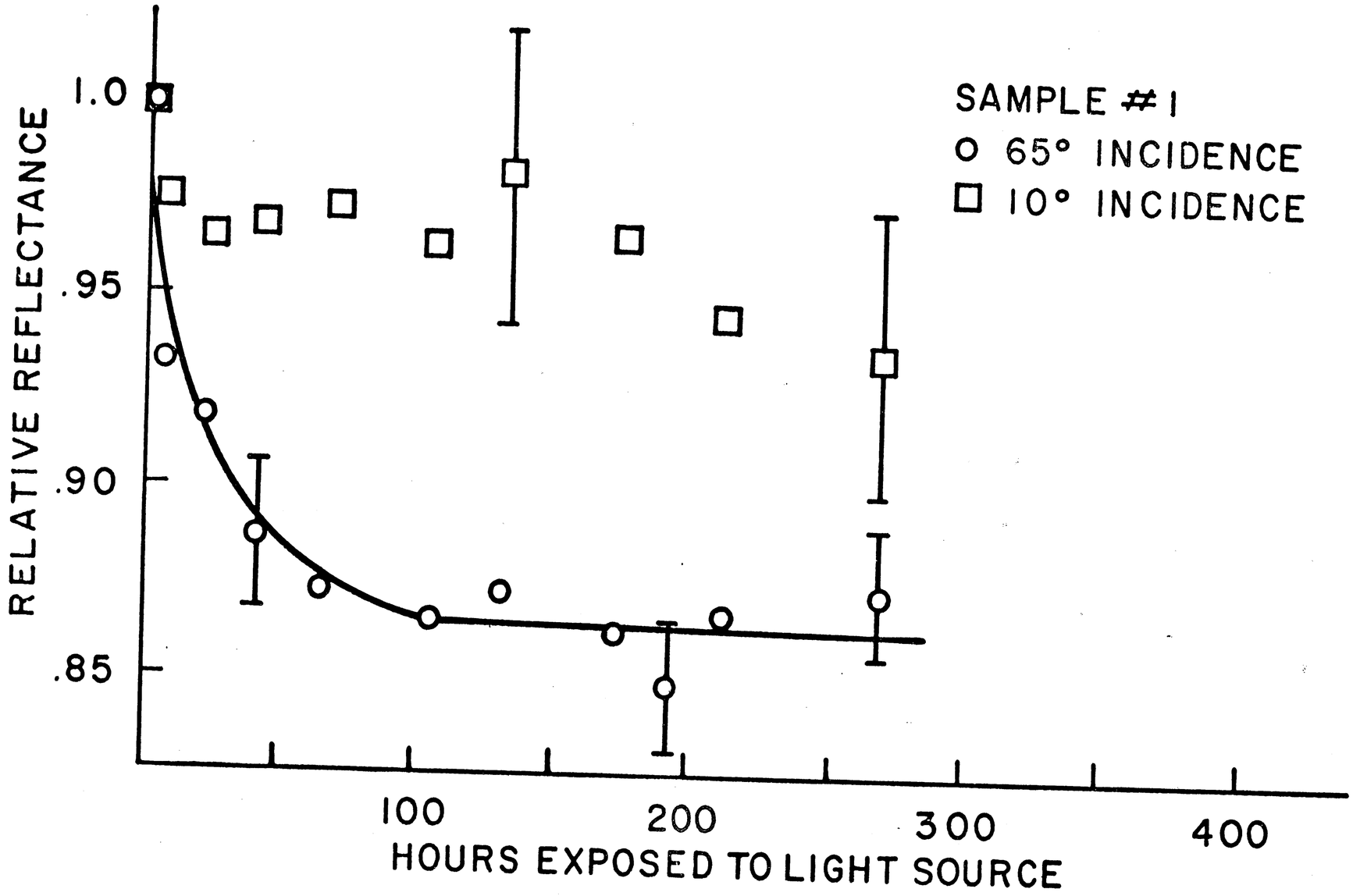

RELATIVE REFLECTANCE
1.0
.95
.90
.85
100
200
300
400
HOURS EXPOSED TO LIGHT SOURCE
SAMPLE #1
65° INCIDENCE
10° INCIDENCE

FIGURE 14

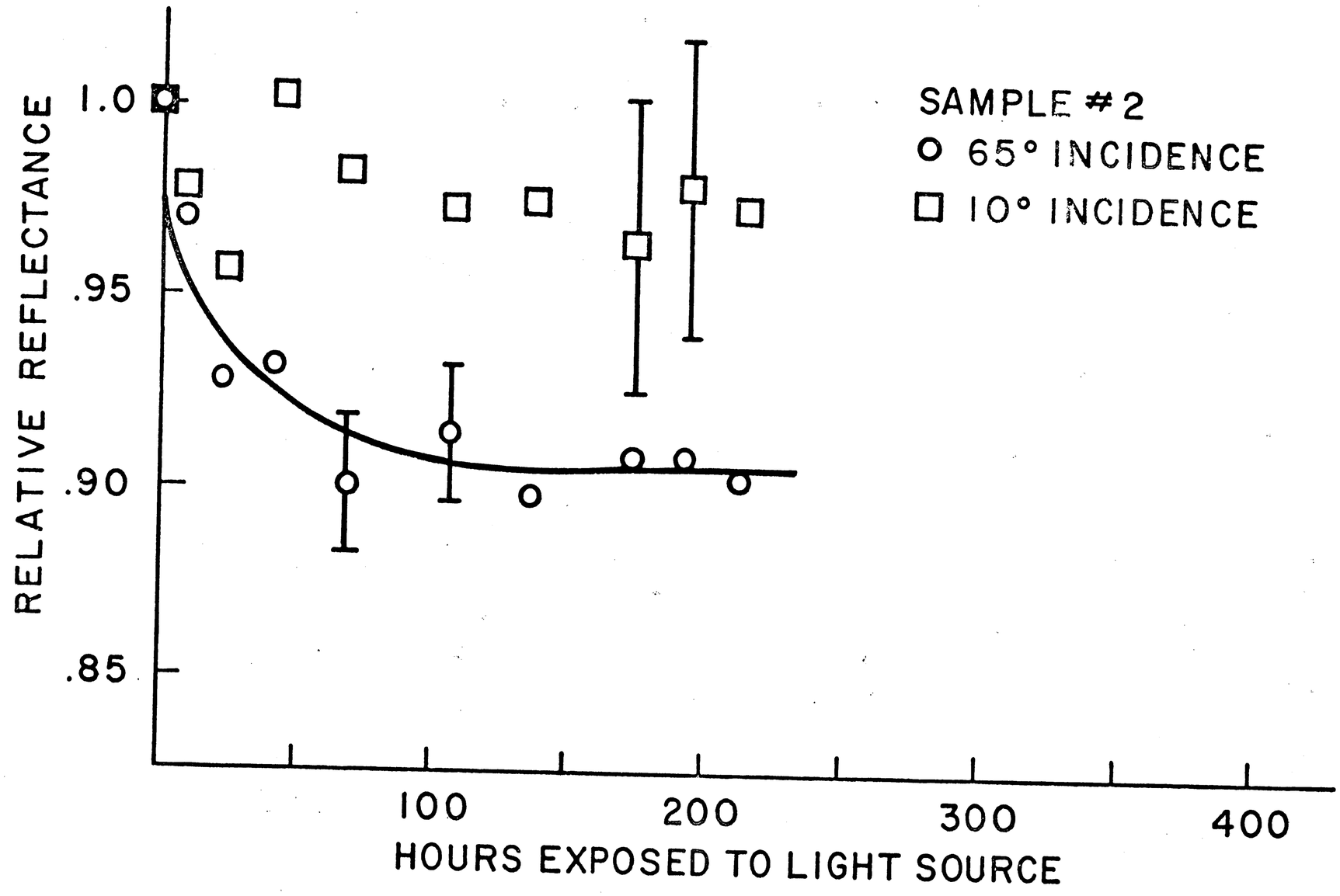

RELATIVE REFLECTANCE
1.0
.95
.90
.85
100
200
300
400
HOURS EXPOSED TO LIGHT SOURCE
SAMPLE #2
65° INCIDENCE
10° INCIDENCE

FIGURE 15

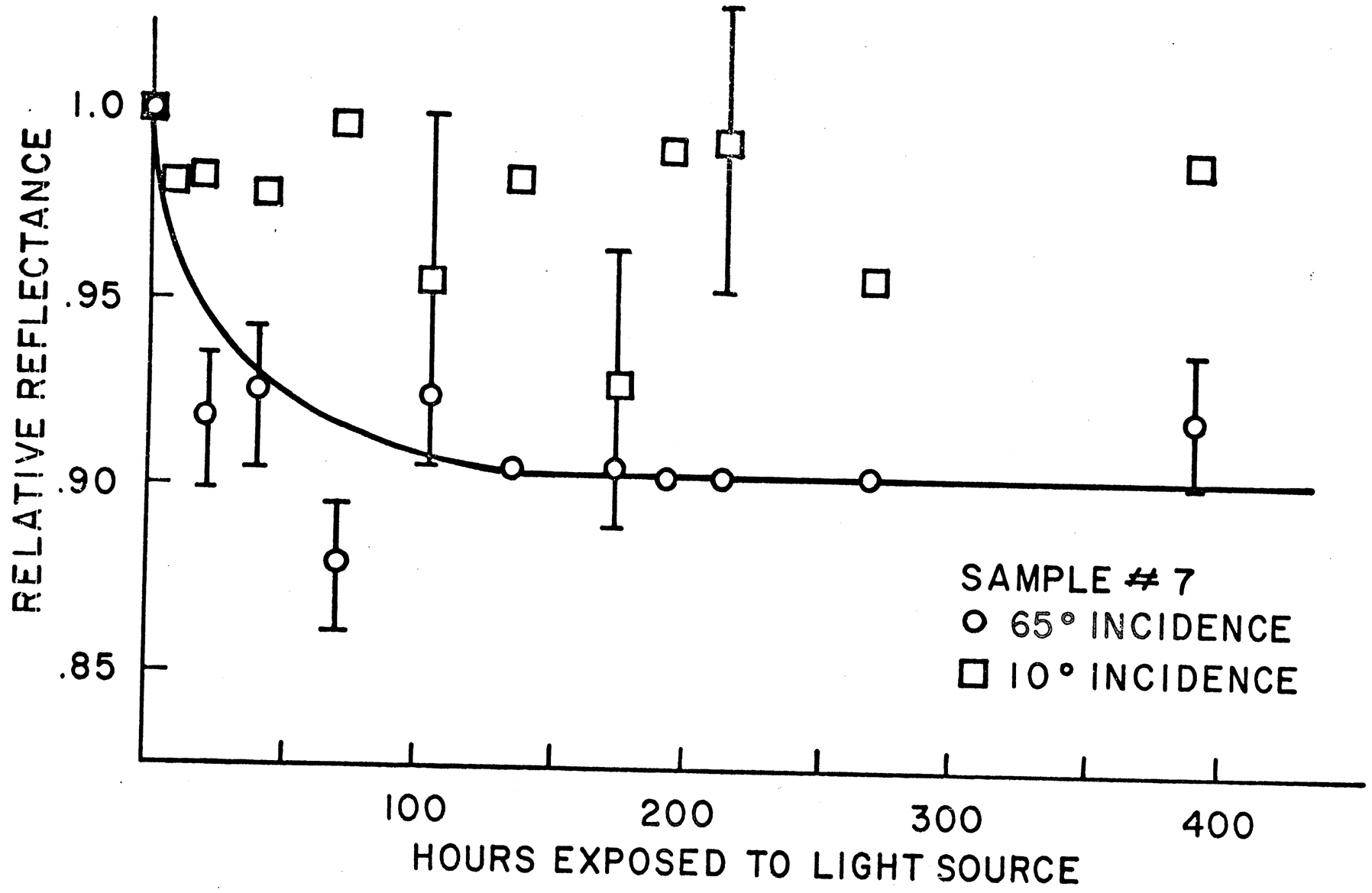
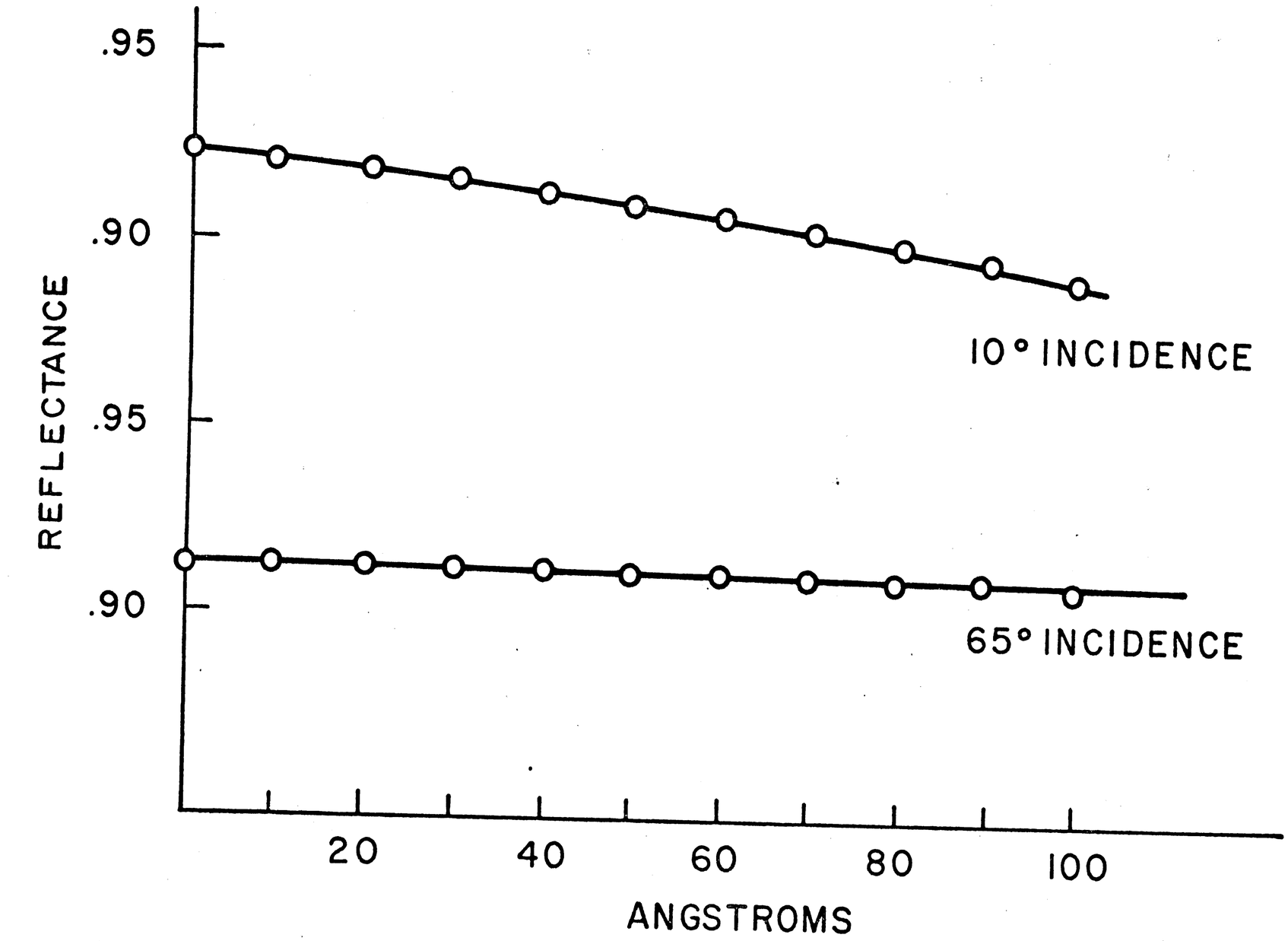

RELATIVE REFLECTANCE
1.0
.95
.90
.85
SAMPLE # 7
65° INCIDENCE
10° INCIDENCE
100
200
300
400
HOURS EXPOSED TO LIGHT SOURCE

FIGURE 16



COMPUTED VALUES OF ABSOLUTE REFLECTANCE VS OXIDE THICKNESS

FIGURE 17

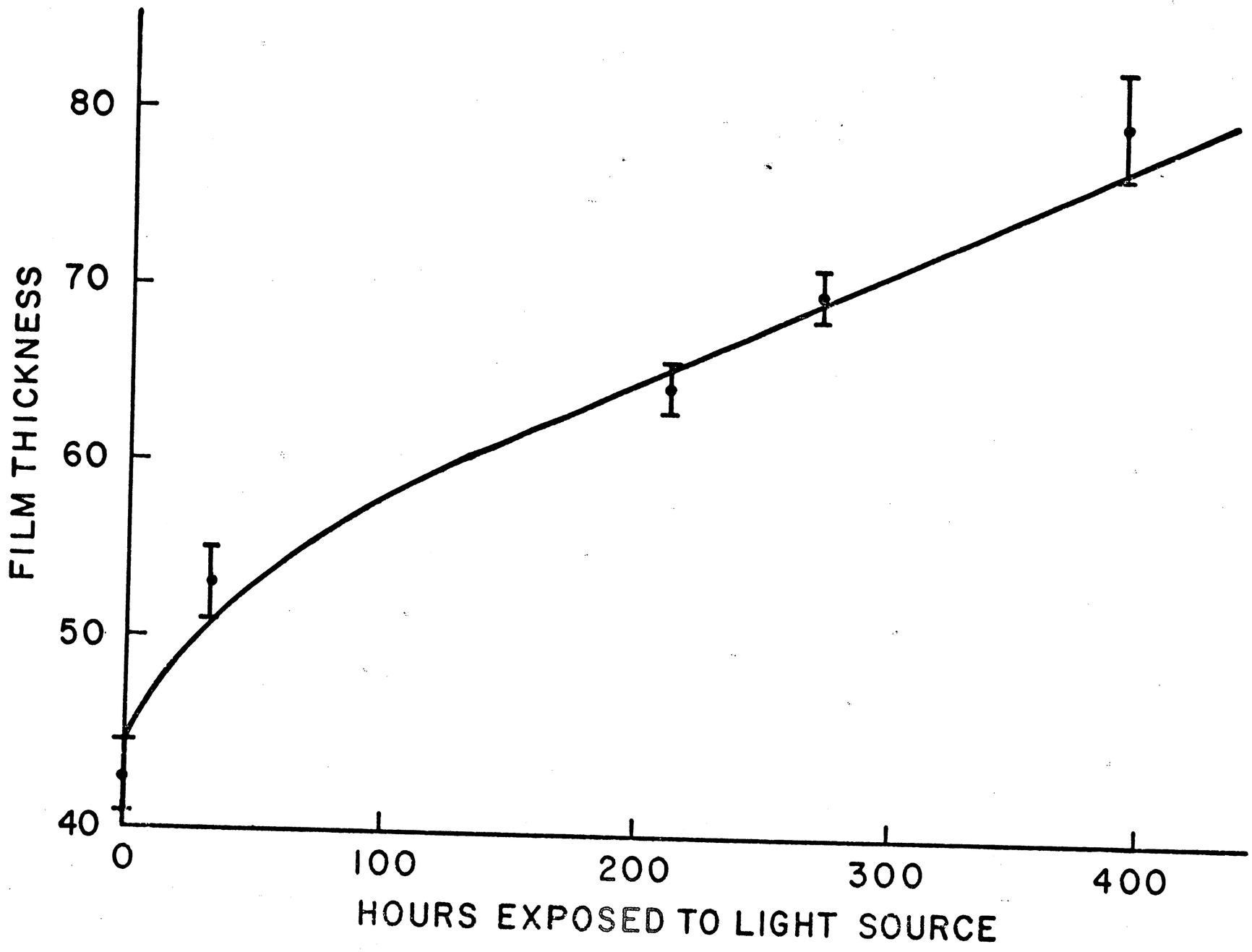

FILM THICKNESS
80
70
60
50
40
0
100
200
300
400
HOURS EXPOSED TO LIGHT SOURCE

FIGURE 18

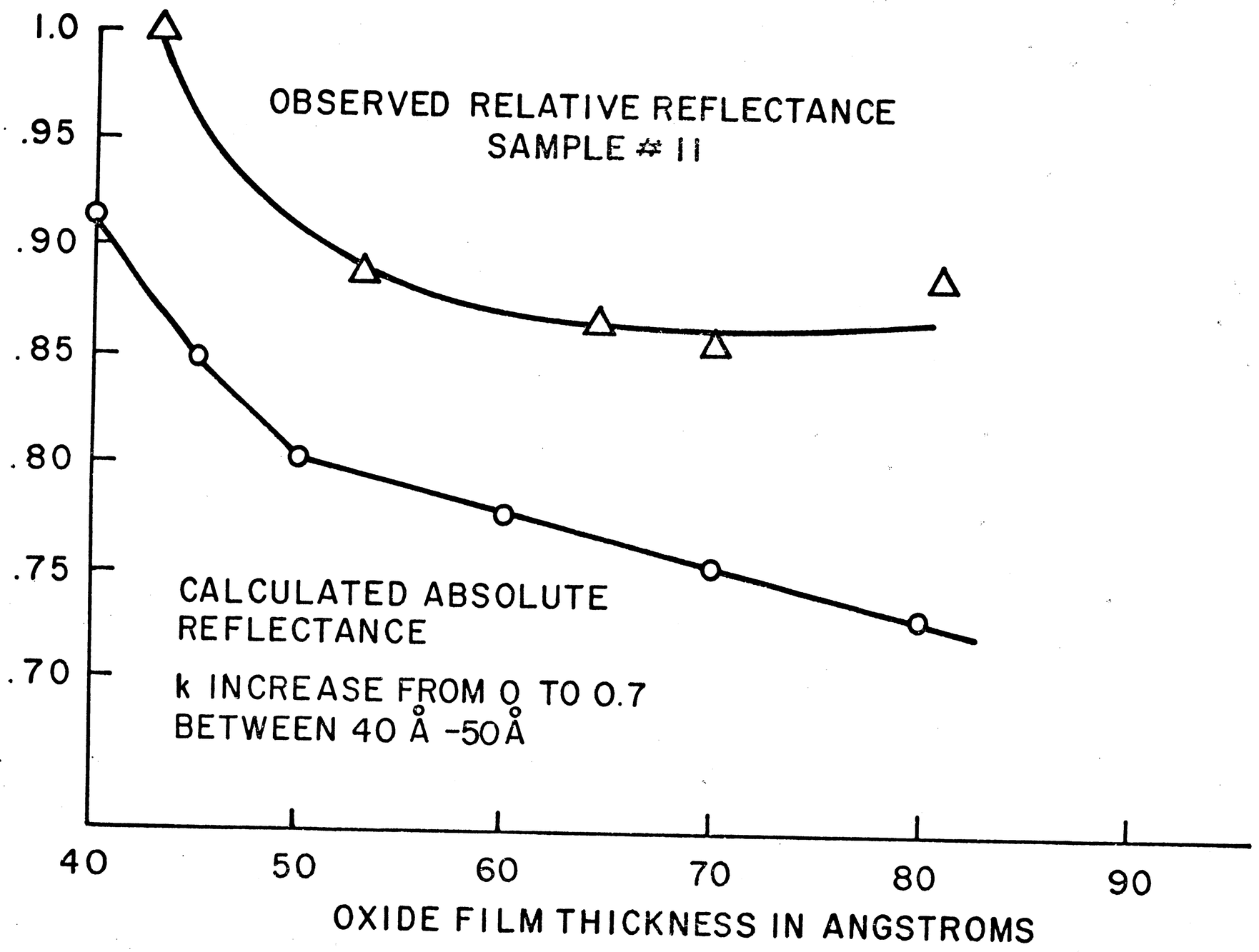

1.0
.95
.90
.85
.80
.75
.70
OBSERVED RELATIVE REFLECTANCE
SAMPLE # 11
CALCULATED ABSOLUTE
REFLECTANCE
k INCREASE FROM 0 TO 0.7
BETWEEN 40 Å -50 Å
40
50
60
70
80
90
OXIDE FILM THICKNESS IN ANGSTROMS

FIGURE 19

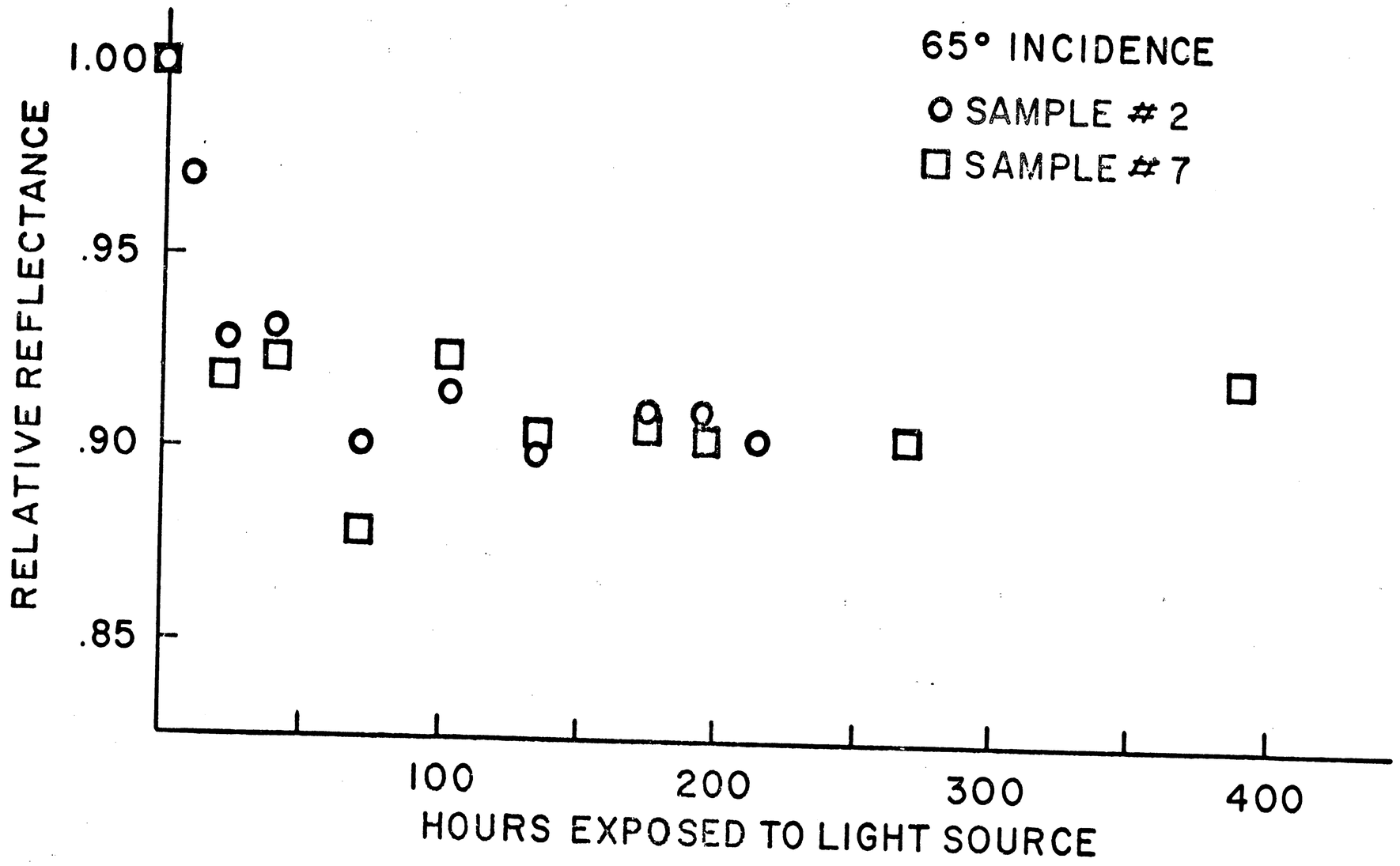

65° INCIDENCE
SAMPLE # 2
SAMPLE # 7
RELATIVE REFLECTANCE
1.00
.95
.90
.85
100
200
300
400
HOURS EXPOSED TO LIGHT SOURCE

FIGURE 20

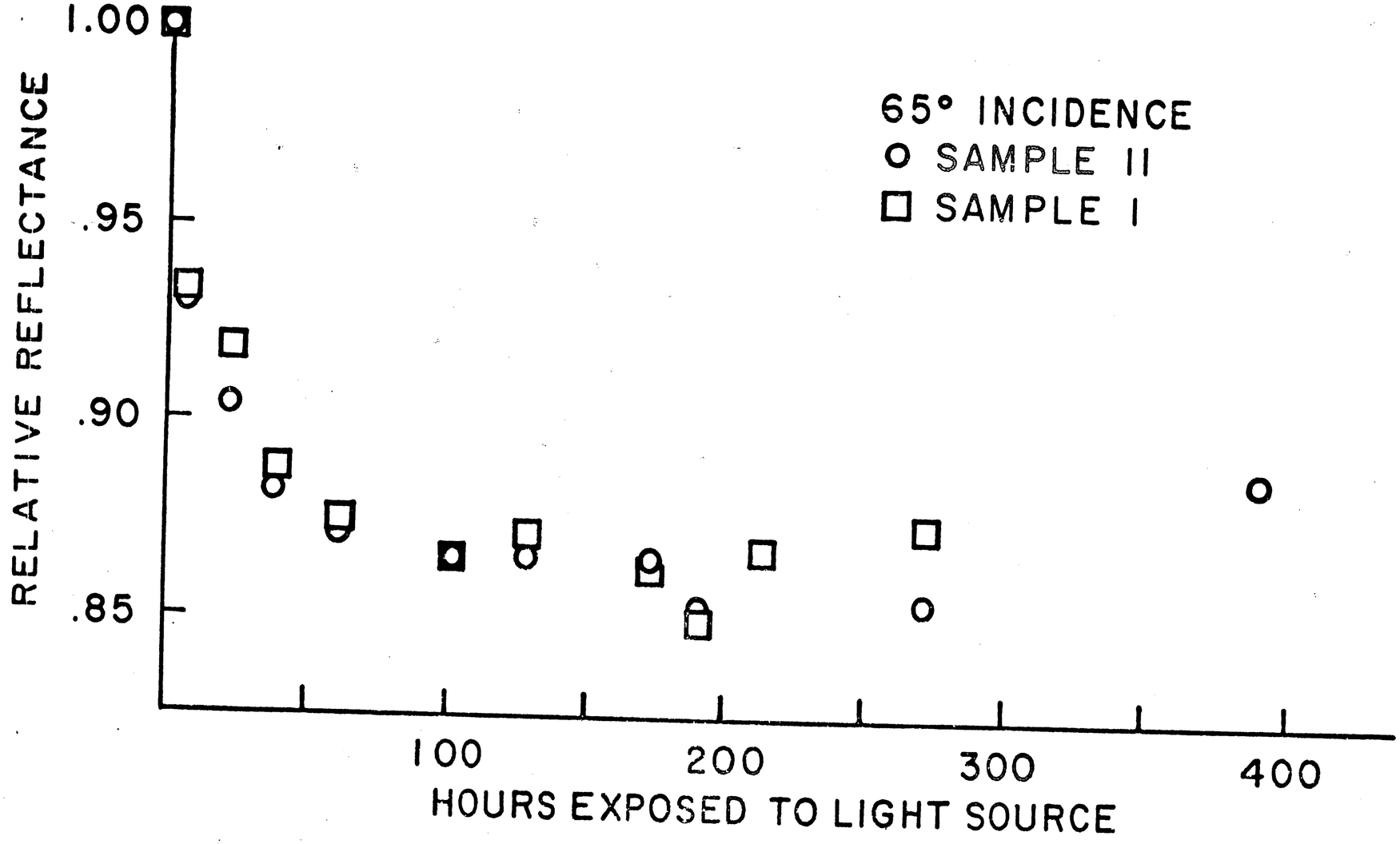
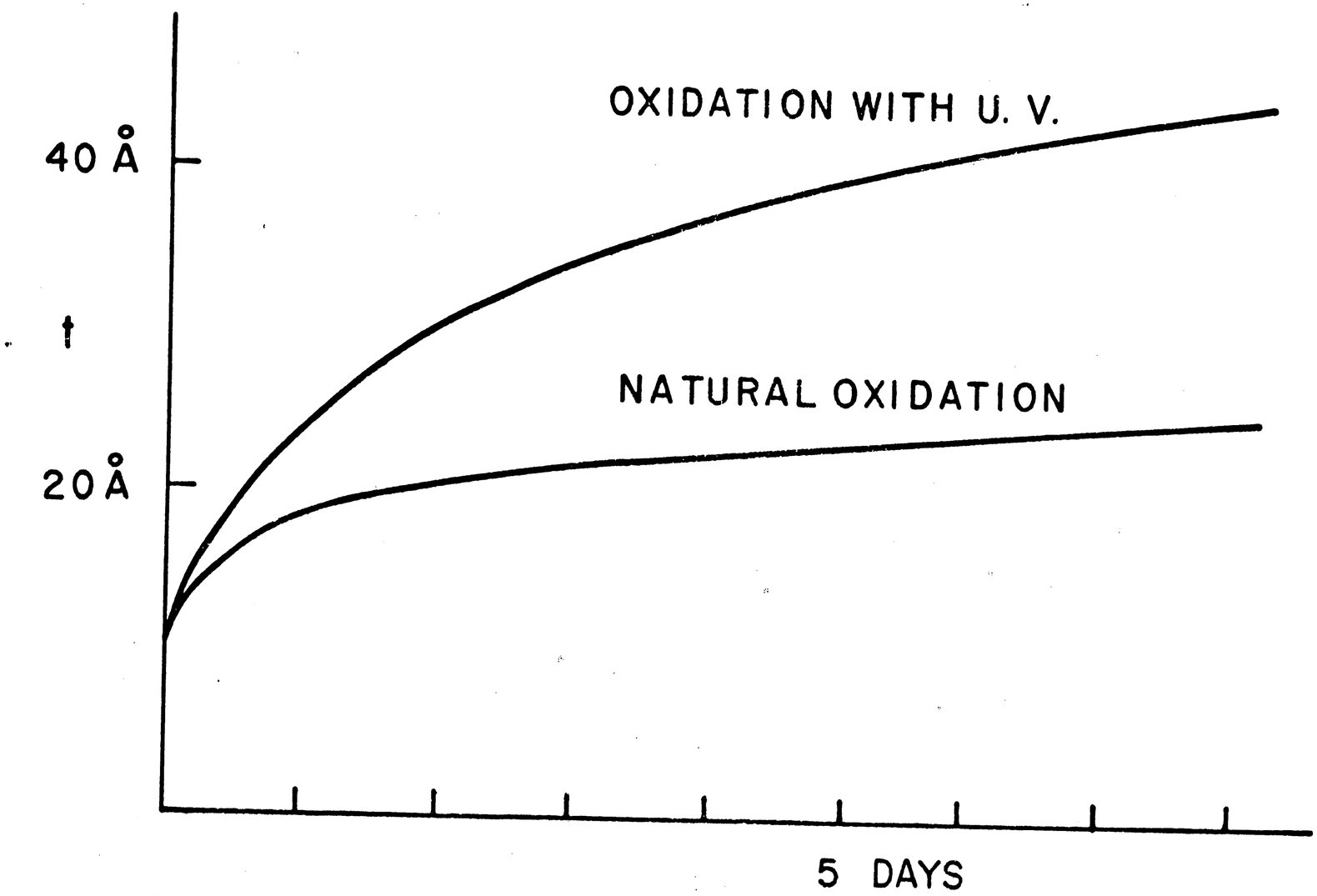
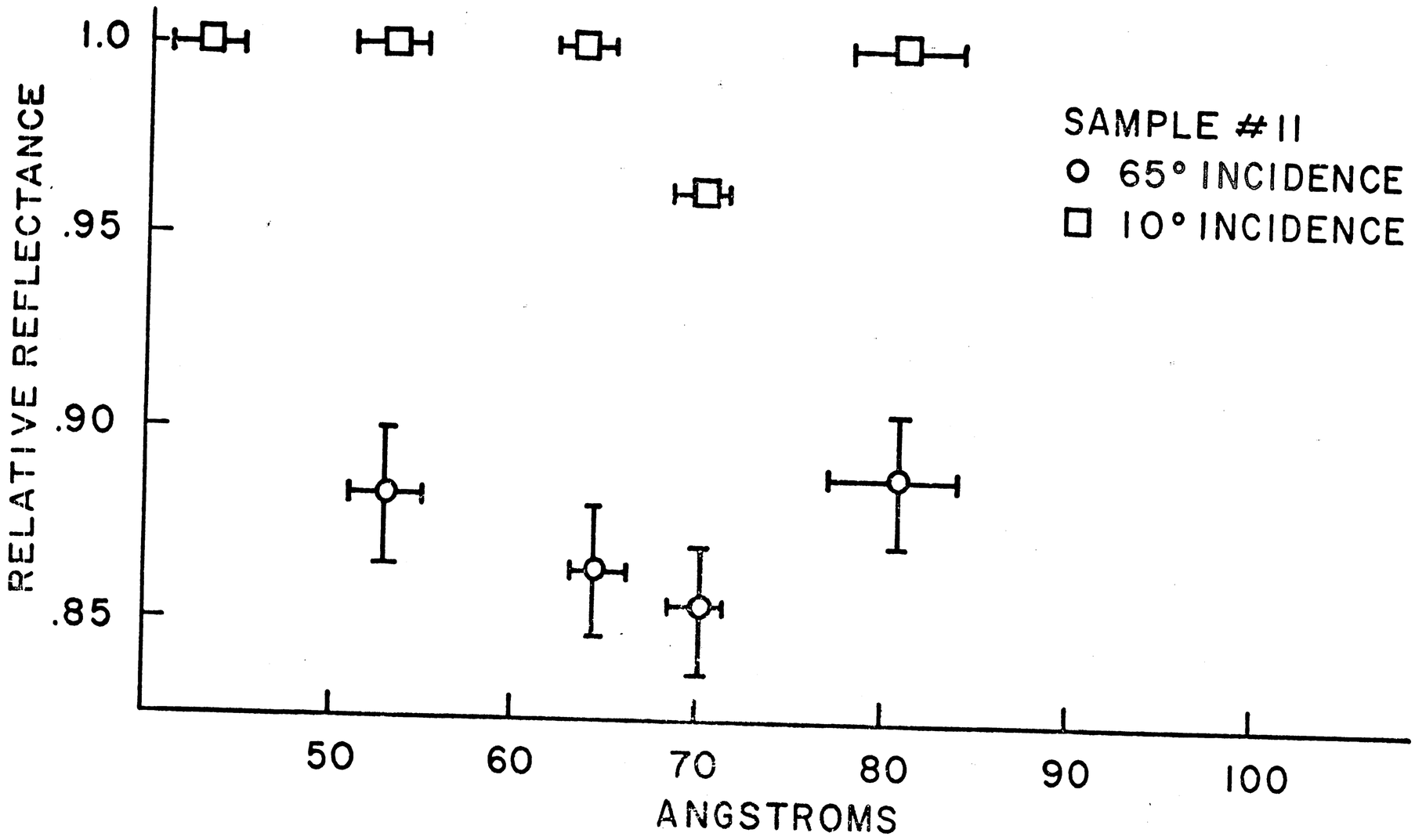

1.00
.95
.90
.85
RELATIVE REFLECTANCE
65° INCIDENCE
SAMPLE II
SAMPLE I
100
200
300
400
HOURS EXPOSED TO LIGHT SOURCE

FIGURE 21



FROM CABRERA REF 13

FIGURE 22



COMPARING REFLECTANCE LOSS WITH OXIDE THICKNESS

FIGURE 23

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VITA

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He entered night school at Youngstown University and was graduated in June 1960 with a Bachelor of Science degree in Physics. Mr. Maselli joined the Western Electric Company in Chicago, Illinois as an engineer in the Systems Equipment Engineering Division.

In June 1969, he became a candidate for the degree of Master of Science in Metallurgy and Material Science at Lehigh University through the Lehigh Masters Program of Western Electric at the Corporate Education Center in Princeton, New Jersey.